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THEIR CHEMISTRY AND METALLURGY

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In diesem Zusammenhang erschien es von besonderem Interesse festzustellen, ob eine Entladung von Uran in Verbindung mit einem geeigneten, entladungsfähigen anderen Metallion als Legierung, wie bei Wolfram und Molybdän^{4,5,6}, oder als Einlagerung einer Uranverbindung niedriger Oxydationsstufe in ein anderes elektrolitisch kristallisierendes Metall möglich ist.

2. THERMODYNAMISCHE AUSSAGEN ZUR ELEKTROLYSE VON URAN AUS WÄSSRIGEN LÖSUNGEN UND ZUR LEGIERUNGSABSCHEIDUNG

Wie die Abstufung der Gleichgewichts-Bezugsspannungen in Tabelle I zeigt, ist bei der wässrigen Elektrolyse von Uransalzen thermodynamisch mit der kathodischen

TABELLE I

ZUSAMMENSTELLUNG DER WICHTIGSTEN ELEKTRODENREAKTIONEN AM STOFFSYSTEM URAN/WÄSSRIGE LÖSUNG BEI 25°C UND DIE pH-ABHÄNGIGKEIT DER GLEICHGEWICHTS-BEZUGSSPANNUNG U_H GEGEN DIE NORMAL-WASSERSTOFFELEKTRODE

Elektrodenreaktion		pH-Abhängigkeit
1. U	$\rightarrow U^{+3} + 3e$	$U_H = (-1.798 + 0.0197 \log a_{U^{+3}})V$
2. $U + 3 H_2O$	$\rightarrow U(OH)_3 + 3 H^+ + 3 e$	$U_H = (-1.346 - 0.0591 \text{ pH})V$
3. $U + 2 H_2O$	$\rightarrow UO_2 + 4 H^+ + 4 e$	$U_H = (-1.444 - 0.0591 \text{ pH})V$
4. $U + 4 H_2O$	$\rightarrow U(OH)_4 + 4 H^+ + 4 e$	$U_H = (-1.353 - 0.0591 \text{ pH})V$
5. $U(OH)_3$	$\rightarrow UO_2 + H_2O + H^+ + e$	$U_H = (-1.738 - 0.0591 \text{ pH})V$
6. $U(OH)_3 + H_2O$	$\rightarrow U(OH)_4 + H^+ + e$	$U_H = (-1.375 - 0.0591 \text{ pH})V$
7. UO_2	$\rightarrow UO_2^{+2} + 2 e$	$U_H = (0.221 + 0.0295 \log a_{UO_2^{+2}})V$
8. $3 UO_2 + 2 H_2O$	$\rightarrow U_3O_8 + 4 H^+ + 4 e$	$U_H = (0.533 - 0.0591 \text{ pH})V$
9. $UO_2 + H_2O$	$\rightarrow UO_3 + 2 H^+ + 4 e$	$U_H = (0.657 - 0.0591 \text{ pH})V$
10. $UO_2 + 3 H_2O$	$\rightarrow UO_3 \cdot 2 H_2O + 2 H^+ + 2 e$	$U_H = (0.386 - 0.0591 \text{ pH})V$
11. $3 U(OH)_4$	$\rightarrow U_3O_8 + 4 H_2O + 4 H^+ + 4 e$	$U_H = (0.260 - 0.0591 \text{ pH})V$
12. $U(OH)_4$	$\rightarrow UO_3 + H_2O + 2 H^+ + 2 e$	$U_H = (0.475 - 0.0591 \text{ pH})V$
13. $U(OH)_4 + H_2O$	$\rightarrow UO_3 \cdot 2 H_2O + 2 H^+ + 2 e$	$U_H = (0.205 - 0.0591 \text{ pH})V$
14. $U_3O_8 + 4 H^+$	$\rightarrow 3 UO_2^{+2} + 2 H_2O + 2 e$	$U_H = (-0.403 + 0.1182 \text{ pH} + 0.0886 \log a_{UO_2^{+2}})V$
15. $U_3O_8 + H_2O$	$\rightarrow 3 UO_3 + 2 H^+ + 2 e$	$U_H = (0.904 - 0.0591 \text{ pH})V$
16. $U_3O_8 + 7 H_2O$	$\rightarrow 3 UO_3 \cdot 2 H_2O + 2 H^+ + 2 e$	$U_H = (0.093 - 0.0591 \text{ pH})V$
17. $e + H^+$	$\rightarrow 1/2 H_2$	$U_H = (0.0 - 0.0591 \text{ pH})V; p_{H_2} = 1 \text{ atm}$
18. H_2O	$\rightarrow 1/2 O_2 + 2 H^+ + 2 e$	$U_H = (1.228 - 0.0591 \text{ pH})V; p_{O_2} = 1 \text{ atm}$

Entladung des UO_2^{2+} -Ions, d.h. mit dem Ablauf der Elektrodenreaktionen 7 und 14 und damit der *Bildung der Oxyde* UO_2 und U_3O_8 zu rechnen. Eine kathodische Abscheidung von *metallischem Uran* aus wässrigen Lösungen wäre wegen der stark negativen Abscheidungsspannung nur bei einer hinreichend hohen Wasserstoffüberspannung oder extrem hohen Stromdichten denkbar. Da jedoch die Wasserstoffüberspannung an Uran und seinen Oxyden, wie auch galvanostatische und potentiostatische Untersuchungen¹ zeigen, für die zur Abscheidung erforderliche kathodische Polarisation nicht ausreicht, wurden zur Klärung dieser Fragen versuchsweise Abscheidungen an Quecksilber, welches selbst über eine hohe Wasserstoffüberspannung verfügt, durchgeführt. Jedoch konnten auch hier, in Übereinstimmung mit der Literatur⁷, keine eindeutigen Ergebnisse erzielt werden. U.a. ergaben Strukturunter-

suchungen des auf der Oberfläche gebildeten schwarzen Pulvers die kubisch flächenzentrierte Struktur von UO_2 ¹.

Da eine Abscheidung von Uran als reines Metall und als Amalgam nicht möglich ist, erhebt sich die Frage nach einer *Legierungsabscheidung* von Uran, ähnlich der von Wolfram und Molybdän^{4,5,6}, welche ebenfalls aus wässrigen Lösungen nicht als reine Metalle, jedoch als Legierungen abgeschieden werden können. Die Auswahl des zur Legierungsabscheidung mit Uran geeigneten Metalls ist einerseits durch die thermodynamischen Forderungen, dass es sich um ein Metall mit möglichst negativer Abscheidungsspannung und ausserdem hoher Wasserstoffüberspannung handeln muss und andererseits durch die Anforderungen, welche sich aus der späteren Verwendung der Legierung ergeben, sehr eingeschränkt. Eine Annäherung der Abscheidungsspannungen liesse sich gegebenenfalls durch spezifisch wirkende Zusätze zum Elektrolyten oder durch Komplexbildung, d.h. Übergang von der Lösungsbindung zur Reaktionsbindung, mit einer entsprechenden Herabsetzung der freien Metallionenkonzentration erreichen. Jedoch zeigt auch hier ein Überblick über die Abscheidungsspannungen der zur Verfügung stehenden Metalle und deren Wasserstoffüberspannung, dass die gleichzeitige elektrolytische Kristallisation beider Komponenten, z.B. Zn und U, zweiphasig nebeneinander, thermodynamisch nicht möglich ist. Notwendigerweise müsste sie bei dem Abscheidungspotential der reinen negativeren Komponente erfolgen. Die hierzu erforderliche negative Polarisation ist jedoch am Zink nicht erreichbar.

Schliesslich wäre die gelegentlich schon bei sehr niedrigen Stromdichten beobachtete gleichzeitige Abscheidung zweier Metalle als *intermetallische Verbindung* oder unter *Mischkristallbildung* noch dann denkbar, wenn die dadurch veränderte Reaktionsaffinität zu einer hinreichend positiveren Abscheidungsspannung, d.h. Verschiebung der Bezugsspannung in Richtung der edleren Komponente führt. In dem hier angeführten Beispiel einer elektrolytischen Legierungsabscheidung von Uran-Zink kann jedoch erfahrungsgemäss eine Mischkristall- oder Verbindungsbildung nicht erwartet werden, da die Abscheidungsspannungen der reinen Komponenten weit auseinanderliegen. Elektrolytisch abgeschiedene Legierungen liegen gewöhnlich nicht im thermodynamischen Gleichgewichtszustand vor. Daher ist oft bei elektrolytisch abgeschiedenen Legierungen keine oder nur eine belanglose Mischkristallbildung festzustellen, auch wenn nach dem Zustandsdiagramm weitreichende Mischkristallbildung auftritt. Umgekehrt können allerdings zwei Metalle unter weitergehender Mischkristallbildung elektrolytisch kristallisieren, auch wenn das Zustandsdiagramm keine Mischkristallbildung kennt^{4,8,9}. Im folgenden Abschnitt 3 sollen diese Fragen experimentell geprüft und insbesondere die Struktur der eingangs erörterten und thermodynamisch zu erwartenden Oxydbildung und die bei der Mitabscheidung von Zn auftretende Art der *Einlagerung* analytisch, mikroskopisch und durch Strukturanalyse festgestellt werden.

3. DIE KATHODISCHE REDUKTION VON URAN(VI)-VERBINDUNGEN IN ZINKHALTIGEN ELEKTROLYTEN; STRUKTURANALYSE DURCH RÖNTGEN- UND ELEKTRONENBEUGUNG, PHOTOMETRISCHE UND RADIOCHEMISCHE UNTERSUCHUNG DER ABGESCHIEDENEN SCHICHTEN

(a) *Elektrodenpräparation und Messtechnik*

Für die vorliegenden Versuche wurden Scheibenelektroden aus Kupfer mit ver-

schraubter Elektrodenhalterung verwendet. Der zur Isolation der Elektrodenrückseite und Halterung verwendete Abdecklack (Decotol coating) wurde eingebrannt und die abgedrehte Stirnfläche der Scheibenelektrode geschliffen, poliert, elektrolytisch entfettet und anschliessend unter konstanten Versuchsbedingungen chemisch geätzt.

Die Elektrodenreaktionen wurden oszillographisch nach einer mehrfach beschriebenen galvanostatischen Messmethode^{10,11,12} durch Vergleich der gemessenen Ruhe-Bezugsspannungen ermittelt¹.

Uranverbindungen wurden versuchsweise mit Zn aus Sulfat-, Acetat- und Fluorboratbädern, teilweise aus galvanischen Zn-Bädern mit erprobten technischen Zusammensetzungen¹³, abgeschieden. Die Elektrolyseprodukte wurden anschliessend in destilliertem Wasser, Aceton und Alkohol gespült und dann getrocknet.

Der Urangehalt dieser elektrolytisch abgeschiedenen Schicht wurde nach DAVENPORT UND THOMASON¹⁴ kolorimetrisch mit Ammoniumthioglykolat in einer 1 cm Messküvette bestimmt und hierzu für die Extinktion eine Eichkurve im Bereich von 0.2–3.2 mg Uran pro 50 ml Messlösung mit einem Kolorimeter Elko II von Zeiss bei 372 m μ aufgenommen. In diesem Bereich ist die gemessene Extinktion proportional der U(VI)-Konzentration und entspricht dem Lambert–Beer'schen Gesetz. Zink wurde komplexometrisch mit einem Dinatriumsalz der Äthylendiamintetraessigsäure als Titriermittel und Eriochromschwarz T als Indikator bestimmt.

Ferner wurde die Aktivitätsrate dieser Schichten nach Abnahme der Elektrodenhalterung im Methan-Durchflusszähler im α + β -Plateau mit einem Al-Filter von 39.2 mg Al/cm² zur Absorption der weichen β -Strahlung und der α -Strahlung bestimmt. Die gemessene Aktivitätsrate wurde überschlagsmässig unter Annahme eines Wirkungsgrades der Messanordnung von 35% und einer spezifischen α -Aktivität von $3.36 \cdot 10^{-7}$ C/g ²³⁸U ($T_{1/2}$ (²³⁸U) = $4.51 \cdot 10^9$ a)¹⁵ und unter Vernachlässigung der 2.3 MeV β -Absorption durch Wägung der Elektrode vor und nach der Elektrolyse in Gewichtsprozent ²³⁸U umgerechnet und diese mit den Ergebnissen aus kolorimetrischen Messungen verglichen.

Zur röntgenographischen Strukturbestimmung wurden von den elektrolytisch abgeschiedenen Schichten Debye–Scherrer-Diagramme aufgenommen, ausgewertet und mit den aus der Literatur entnommenen Netzebenenabständen¹ der in Frage kommenden Metalle und Verbindungen verglichen. Zur Kontrolle wurden ebenfalls Aufnahmen am reinen Trägermaterial durchgeführt.

Neben der röntgenographischen Strukturanalyse wurden Elektronenbeugungsdiagramme im Elektronendiffraktograph und im Elektronenmikroskop aufgenommen. Ferner wurden zur Vermeidung der durch die Pulverherstellung gegebenen Oxydationsmöglichkeit ebenfalls Aufnahmen bei streifender Beugung an polierten Elektrodenoberflächen gemacht. Die Reinigung und Ätzen der Oberfläche erfolgte durch Ionenbeschuss unter Argon mit einer Ionenätzapparatur im Elektronendiffraktograph. Zur Kühlung wurde flüssiger Stickstoff verwendet.

Zur Herstellung von Oberflächen- und Querschliffen für mikroskopische Untersuchungen wurden die Scheibenelektroden in ein kalthärtendes Polyestergiessharz Leguval eingebettet und in einer glove box geschliffen und poliert. Alle metallographischen Arbeitsgänge der Schliffherstellung und Pulverisierung wurden in einer glove box unter nachgereinigtem Stickstoff durchgeführt. Anschliessend wurden die Schliffe mikroskopisch untersucht und aufgenommen und dabei insbesondere die Einschlüsse im polarisierten Licht auf Doppelbrechung geprüft.

(b) *Uran-Zink-Abscheidung aus Acetatbädern; Diskussion der Messergebnisse, Beugungsaufnahmen und mikroskopischen Untersuchungen*

Die Uran-Zink-Abscheidung auf Cu-Scheibenelektroden aus Acetatbädern führte zu metallischen Zn-Schichten mit einer gleichmässigen Einlagerung von Uranoxyden mit den in Tabelle II zusammengestellten Analysendaten. Die röntgenographischen Untersuchungen ergaben, wie aus den Debye-Scherrer-Diagrammen in Abb. 1

TABELLE II

AKTIVITÄTSRATEN UND ANALYSENDATEN DER URAN-ZINK-ABSCHIEDUNG AUS ACETATBÄDERN

Probe	UO ₂ -Ac g/l	Zn-Ac g/l	U g/l	Zn g/l	kath. Strom- dichte mA/cm ²	Ladung Coul/cm ²	A _R (β, UX ₂) Imp/Min. cm ²	²³⁸ U mg/cm ²	Gew. % Uran kolori- metrisch	Gew. % Zink komplexo- metrisch	Rest in Gew.-%
1	71.2	67.2	40	20	2.5	1116	4150	16	14.9	82.5	2.6
2	71.2	67.2	40	20	2	810	4886	18.9	21.8	75.1	3.1

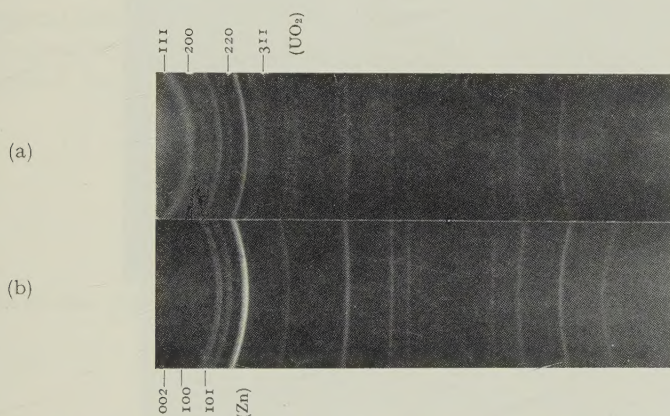


Abb. 1. (a) Röntgenaufnahme einer Uran-Zink-Abscheidung aus einer wässrigen Lösung von Uranyl-Zink-Acetat; Einlagerung von kubisch flächenzentriertem UO₂ in metallischem Zink. (b) Röntgenaufnahme der hexagonalen Struktur von Zink (Cu-K_α-Strahlung mit Ni-Filter).



Abb. 2. Elektronenbeugungsaufnahme einer UO₂-Einlagerung in metallischem Zink; Aufnahme enthält die kubisch flächenzentrierte Struktur von UO₂.

ersichtlich, neben dem hexagonalen Gitter des Zinks eindeutig einen kubisch flächenzentrierten Anteil von UO_2 . Diese Ergebnisse konnten durch die Elektronenbeugungsaufnahme in Abb. 2 bestätigt werden. Wie aus der bei streifender Beugung nach Ionenätzung im Diffraktographen aufgenommenen Elektronenbeugungsaufnahme in Abb. 3 ersichtlich, sind neben UO_2 auch Andeutungen für U_3O_8 vorhanden. Der Mikroschliff in Abb. 4 zeigt, dass die Uranoxyde sehr gleichmässig in das Grundmetall eingelagert sind. Unter der Annahme, dass es sich bei den in Tabelle II verzeichneten restlichen Gewichtsprozenten nur um den im Oxyd gebundenen Sauerstoff handelt, würde sich bei beiden Proben für UO_2 ein zu grosser und für U_3O_8 ein zu kleiner

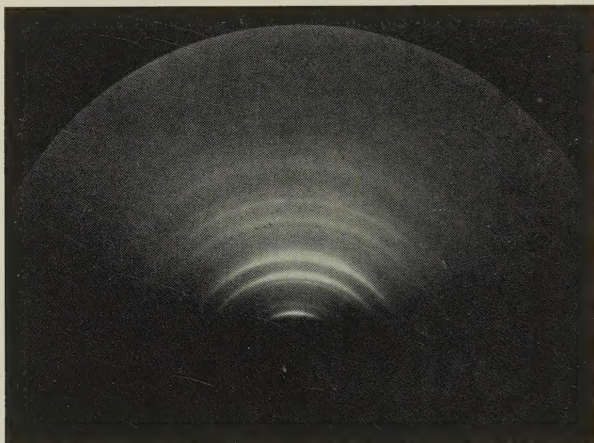


Abb. 3. Elektronenbeugungsaufnahme nach Ionenätzung im Diffraktographen mit streifender Beugung.

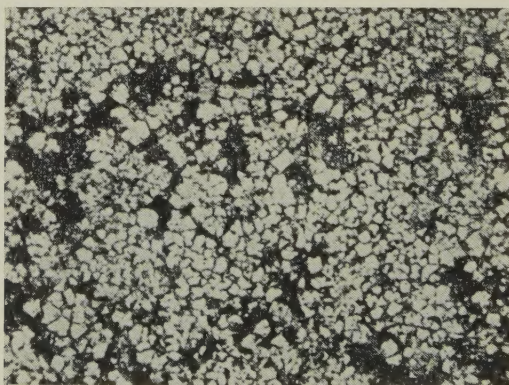
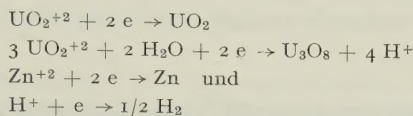


Abb. 4. Mikroschliff einer Zinkschicht mit Einlagerung von UO_2 . ($\times 300$)

Urangehalt ergeben. Bei einer Abschätzung der Oxydanteile an UO_2 , U_3O_8 und u. U. auch $\text{UO}_3 \cdot x\text{H}_2\text{O}$ ¹⁶ ist jedoch die durch Adsorption zu erwartende Einlagerung von Fremdstoffen zu berücksichtigen. Die Streuung der Gewichtsanteile Uran pro Abscheidung unter konstanten Bedingungen betrug $\pm 4\%$. Eine genauere Reproduzier-

barkeit der abgeschiedenen Uranmengen kann an einer Mehrfachelektrode mit mindestens 4 verschiedenen kathodischen Teilströmen der Elektrodenreaktionen



nicht erwartet werden.

Die kolorimetrische Analyse und die Messung der Aktivitätsrate im Methan-Durchflusszähler ergaben mit zunehmender Stromdichte übereinstimmend eine Abnahme des Urangehalts der abgeschiedenen Schichten.

(c) *Uran-Zink-Abscheidung aus Fluoboratbädern; Diskussion der Messergebnisse, Beugungsaufnahmen und mikroskopischen Untersuchungen*

Die Uran-Zink-Abscheidungen aus Fluoboratbädern ergaben im Vergleich zu den vorstehend beschriebenen Abscheidungen aus Acetatbädern Zink-Schichten mit einer gleichmässigen Einlagerung von Urantetrafluorid UF_4 mit einem erheblich höheren Urangehalt bis 46 Gewichtsprozent Uran und 10-fachen Aktivitätsraten.

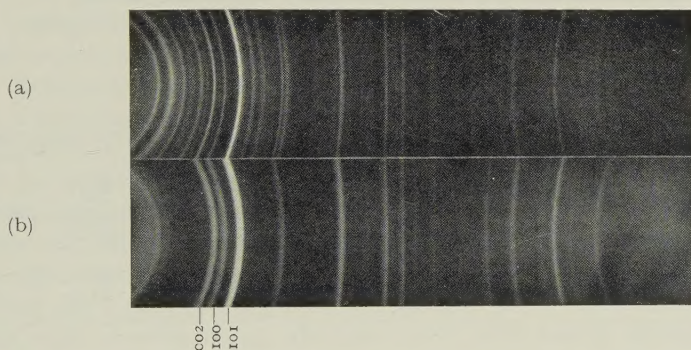


Abb. 5. (a) Röntgenaufnahme einer Uran-Zink-Abscheidung aus einem Fluoboratbad mit Einlagerung von Urantetrafluorid UF_4 in metallischem Zink; (b) Zum Vergleich Röntgenaufnahme einer Zink-Abscheidung aus dem gleichen Fluoboratbad, jedoch ohne Uransalze (Cu- K_α -Strahlung mit Ni-Filter).

Die Debye-Scherrer-Diagramme in Abb. 5 enthalten neben dem hexagonalen Zn-Gitter die aus der ASTM-Kartei entnommene monokline Struktur von UF_4 . Die Aufnahme eines Mikroschliffs in Abb. 6 zeigt die gleichmässige Einlagerung von UF_4 im Grundmetall. Die mikroskopischen Untersuchungen im polarisierten Licht ergaben eine starke Doppelbrechung.

Die bei Probe 1, Tabelle III aus der gemessenen Aktivitätsrate, $A_R = 46\,666$ Imp/Min. $\cdot$ cm ^{2} , abgeschätzte Gewichtsmenge von 0.18 g Uran/cm ^{2} zeigt, dass pro Abscheidung (geometrische Elektrodenoberfläche 6.3 cm ^{2}) mehr als 1 g Uran in Form von UF_4 nach Abb. 6 gleichmässig in Zn eingelagert wurde. Die Annahme, dass entsprechend der röntgenographischen Strukturanalyse alles in Tabelle III angegebene kolorimetrisch bestimmte Uran als UF_4 vorliegt, stimmt bis auf einen kleinen, der

Fremdstoffeinlagerung zuzuschreibenden Rest, gut mit der komplexometrischen Bestimmung von Zn und damit dem in Tabelle III in Gewichtsprozenten angegebenen Restbetrag überein. Ähnlich den Abscheidungen aus Acetatbädern nimmt auch hier mit abnehmender Stromdichte die in Zink eingelagerte Gewichtsmenge UF_4 zu.

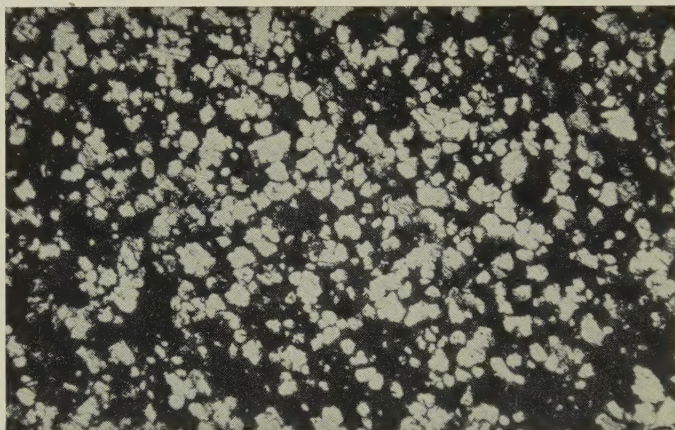


Abb. 6. Mikroschliff einer Zinkschicht mit einer Einlagerung von UF_4 . ($\times 200$)

TABELLE III

AKTIVITÄTSRATEN UND ANALYSENDATEN DER URAN-ZINK-ABSCHIEDUNG AUS FLUOBORATBÄDERN

Probe	$UO_2\text{-Ac}$ g/l	Zn- (BF_4) ₂ g/l	U g/l	Zn g/l	kath. Strom- dichte mA/cm ²	Ladung Coul/cm ²	$Az(\beta, UX_2)$ Imp/Min. cm ²	²³⁸ U mg/cm ²	Gew. % Uran kolori- metrisch	Gew. % Zink komplexo- metrisch	Rest in Gew.-%
1	89	183	50	50	2.5	1100	46 666	180	46	38.1	15.9
2	89	183	50	50	5	1100	28 415	110	35.4	52.7	11.9

4. BISHERIGE VERFAHREN DER URAN-SCHMELZFLUSSELEKTROLYSE UND IHRE ANWENDBARKEIT

Nach einer thermodynamischen Erörterung und experimentellen Klärung der Abscheidung von Uranverbindungen aus wässrigen Lösungen, insbesondere Acetat- und Fluorboratbädern, werden in diesem Abschnitt die bisherigen Verfahren der elektrolytischen Abscheidung von metallischem Uran aus Salzschnmelzen kurz zusammengestellt* und ihre Anwendbarkeit z.B. auf die Reindarstellung von Uran^{18,19,20}, Aufbereitung von Brennelementen^{21,22,23} und Uranrückständen²², insbesondere Uranoxyden^{22,24-27} besprochen.

Ähnlich den pyrometallurgischen und pyrochemischen Prozessen^{28,29,30} führt auch die Schmelzflusselektrolyse unmittelbar zum metallischen Zustand. Wie weit zur Schmelzflusselektrolyse als Ausgangsprodukt ein Uran-Halogenid, Oxyd, Carbide oder

* Eine Zusammenstellung der älteren Literatur ist in der Arbeit von MARDEN, LILIENDAHL, MEISTER, NAGY, WROUGHTON UND BEESE¹⁷ enthalten.

metallisches Uran geeignet ist, hängt ebenso wie das bei der Elektrolyse entstehende Kathodenprodukt z.B. ein Dendritenwachstum oder eine metallische Schmelze, im wesentlichen von dem dabei verwendeten Raffinationsverfahren ab.

Die bisherigen Verfahren lassen sich nach den folgenden Gesichtspunkten zusammenstellen:

(a) Schmelzflusselektrolyse *an Luft*^{31,32} in ausschliesslich wasserunlöslichen Salzen, wobei die Schmelze eine Oxydation des Metallniederschlags verhindern soll

(b) Schmelzflusselektrolyse u.a. auch in wasserlöslichen oder sogar hygroskopischen Salzen unter Inertgas in *geschlossenen* Gefässen

(c) Verwendung einer *unlöslichen* Anode, z.B. Graphitanode, mit anodischer Gasentwicklung (z.B. Cl_2) bei kathodischer Uranabscheidung. Die Uranzufuhr erfolgt dabei durch Auflösen einer geeigneten Uranverbindung, meist ein Halogenid z.B. UCl_3 ^{16,18,19,20}, UCl_4 ^{16,33}, UF_4 ^{16,31,33}, K_2UF_6 ^{17,31,34,35}, KUF_5 ^{17,31,32,33}, UI_3 ³⁶ und UBr_3 ³⁷ oder auch Oxyd^{22,24,25,26,27} oder UC_2 ^{38,39} etc. in einem Alkali- oder Erdalkali-halogenidbad z.B. NaCl und CaCl_2 ^{20,32,33,40}, LiCl und KCl ^{19,41}, BaF_2 und MgF_2 ²⁴ und LiF und NaF ⁴², letztere mit ausreichend negativen Abscheidungsspannungen.

(d) Verwendung einer *löslichen*, metallischen Urananode, welche entsprechend der kathodischen Uranabscheidung anodisch in Lösung geht⁴³

(e) Schmelzflusselektrolyse *oberhalb* des Schmelzpunktes von Uran (1133°C)¹⁶ mit einem geschmolzenen Endprodukt^{24,26,27,44}

(f) Schmelzflusselektrolyse *unterhalb* des Uran-Schmelzpunktes mit kathodischer Dendritenbildung^{18,19,33,34,41,44}

(g) Kontinuierliches Verfahren^{22,24,26,27,45} oder Einzelabscheidung^{18,34,44}

(h) Verwendung niederschmelzender Uran-Legierungen^{21,38} um ein geschmolzenes Endprodukt bereits unterhalb des Uran-Schmelzpunktes zu erhalten.

Die Auswahl eines geeigneten Verfahrens richtet sich nach den jeweils vorliegenden Erfordernissen. So wird der Betrieb einer Raffinationszelle *oberhalb* des Uranschmelzpunktes mit einem geschmolzenen Endprodukt einen *kontinuierlichen* Betrieb der Zelle begünstigen, wogegen die *laufende Kontrolle* einer Elektrolyse durch die erst *unterhalb* des Uran-Schmelzpunktes möglichen festen kathodischen Einzelabscheidungen einer Anodencharge erleichtert wird. Gleichzeitig entfällt durch Auswahl eines geeigneten niederschmelzenden Eutektikums das ungleich schwierigere Materialproblem bei hohen Temperaturen. Andererseits ist die Entnahme hoch radioaktiver Produkte im geschmolzenen Zustand u.U. leichter durchzuführen, als dies bei Dendriten mit dem in Anschluss an die Elektrolyse erforderlichen Auslaugen der Badeinschlüsse und Einschmelzen der Kathodenprodukte^{17,18,19,41,46} der Fall ist.

Die elektrolytische Reinstdarstellung von Uran kann, wie die Arbeiten von BLUMENTHAL UND NOLAND¹⁸ und MARZANO^{19,45} zeigen, zu nahezu spektralreinem Uran mit maximal 70 p.p.m. Gesamtverunreinigung führen. Wie der Bericht von BLUMENTHAL UND BRODSKY⁴⁷ auf der internationalen Konferenz über die Metallurgie des Plutoniums in Grenoble zeigte, konnte dieser Reinheitsgrad inzwischen auch bei Plutonium erzielt werden.

Nach NIEDRACH⁴⁴ ist die Schmelzflusselektrolyse zur Aufbereitung kurz gekühlter metallischer Brennelemente und schnellen Rückführung in den Reaktor geeignet, da die verwendeten Bäder und Materialien sehr beständig gegen Strahlenschäden sind. Gegenüber den pyrochemischen Prozessen findet nicht nur eine Dekontamination der chemisch aktiveren metallischen Spaltprodukte, sondern gleichzeitig auch der edleren

Spaltprodukte statt. Die edleren Spaltprodukte werden dabei anodisch nicht aufgelöst, sondern verbleiben im Anodenschlamm, während die unedleren Spaltprodukte, d.h. die stabileren Verbindungen mit einer grösseren Bildungsaffinität A (negativeren freien Bildungsenthalpie $-\Delta G = A$) anodisch in Lösung gehen und kathodisch mit abgeschieden werden, sofern ihre Bildungsaffinität nicht so gross ist, dass die zur Abscheidung erforderliche Bezugsspannung der entsprechenden Elektrodenreaktion unterhalb der an der Kathode eingestellten Bezugsspannung liegt. Solche aktiven Metalle (Alkali, Erdalkali, Seltene Erden) werden nicht abgeschieden, sondern verbleiben im Bad und ergeben damit wieder eine gute Trennung. Der bessere Dekontaminationsfaktor gegenüber pyrochemischen Prozessen ist jedoch hier mit komplizierteren Ausrüstungs- und Arbeitsbedingungen verbunden.

NIEDRACH UND DEARING^{22,24,26}, SCHÄFER²⁷ und COFFMANN²⁵ zeigten ferner, dass auch Uranoxyde, besonders UO_3 , aber auch UO_2 und U_3O_8 durch die Schmelzflusselektrolyse, insbesondere durch ein kontinuierliches Verfahren oberhalb des Uranschmelzpunktes, bei etwa 1200°C , unmittelbar zum Metall reduziert werden können und damit der Umweg über die Herstellung von UF_4 und Reduktion mit Ca oder Mg in geschlossenen Druckbomben entfällt. NIEDRACH, DEARING UND SCHÄFER²⁷ gaben wirtschaftliche Überlegungen für eine Raffinationsanlage, welcher sie eine Tagesproduktion von 10 Tonnen Uran zugrundelegten, an.

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THE SURFACE ENERGY OF SOLID NIOBIUM

S. V. RADCLIFFE

Research Division, Manufacturing Laboratories, Inc., Cambridge, Mass. (U.S.A.)

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SUMMARY

The surface energy of solid niobium has been measured by a modification of the wire method utilizing an electron-bombardment heating technique. At 2250°C the surface energy is 2100 ergs cm⁻². This result is consistent with a theoretical estimate. From measurements of the dihedral angle of grain boundary grooves formed by thermal etching, the grain boundary interfacial energy of niobium is computed to be 0.36 of the surface energy.

INTRODUCTION

A knowledge of the surface energy of the refractory metals is important for the understanding of a number of metallurgical phenomena involved in applications of these materials. In particular, surface energy provides the driving force for densification during the sintering process¹ and is of importance in cleavage fracture², catalysis and corrosion³.

Although there are several calculations and estimates of the surface energy of liquid refractory metals^{4,5}, experimental measurements are available only for liquid tungsten at its melting point⁶. No surface energy values have been reported for solid refractory metals.

Methods that have been used to measure the surface energy of crystalline solids are: (a) comparison of the heats of solution of large and small particles⁷; (b) measurement of the energy required to cleave a crystal⁸; and (c) measurement of the force required to balance the surface tension of a small diameter wire at temperatures near the melting point. Method (a) suffers from difficulties associated with obtaining fine particles free from strain and with measuring the surface area of the particles. For metals, method (b) has limited application in that many pure metal crystals are so ductile, even at low temperatures, that cleavage cannot be induced. Method (c) can be used only at high temperature and does not yield values for individual crystallographic faces. However, despite its limitations, the latter method, which was developed by UDIN and co-workers, has been applied successfully to copper⁹, silver¹⁰, gold¹¹ and nickel¹².

The work described here concerns the application of a modification of the wire method to the measurement of the surface energy of solid niobium.

EXPERIMENTAL METHOD

At temperatures near the melting point, freely suspended small diameter wires of many metals will contract due to the stresses produced by surface energy forces. The

rate of contraction is determined by the unbalance between the opposing forces of the surface tension and the load on the wire. The surface energy of the wire material can be computed from a knowledge of the value of the load which causes the strain rate to be zero.

For polycrystalline wires in which the grains occupy the whole cross-section of the wire and the grain boundaries lie in planes normal to the wire axis (the so-called "bamboo" structure), UDIN¹³ has shown that the effect of the surface energy of the grain interfaces on the balance of forces can be expressed as:

$$\omega = \pi r \gamma - n \pi r^2 \gamma' \quad (1)$$

where ω is the load required to balance the surface energy force, r the wire radius, γ the surface energy, n the number of grains per unit length of the wire and γ' the grain boundary interfacial energy. The value of the grain boundary energy can be determined¹⁴ from measurement of the dihedral angle at grain boundary grooves developed at the specimen surface by thermal etching. At equilibrium between the forces at the free surface and the grain boundary interfaces:

$$\gamma' = 2 \gamma \cos \frac{\theta}{2} \quad (2)$$

The principal problem in the application of the wire method to the measurement of the surface energy of refractory metals is the provision of a heat source suitable for operating at temperatures greater than 2000°C and an atmosphere which does not contaminate these reactive materials. In the present application to niobium, suitable micro-creep experiments have been carried out on single specimen wires by the use of an electron-bombardment furnace operated at high vacuum.

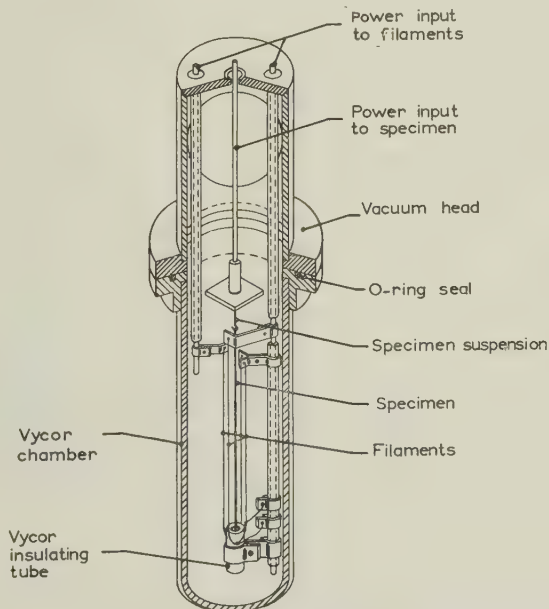


Fig. 1. Electron-bombardment apparatus for the measurement of the surface tension of solid metals.

Specimens were made from cold-drawn wire, 0.025 in. in diameter. The purity of the material, which was supplied by the Fansteel Metallurgical Corporation, was better than 99.8%. Each specimen consisted of a 6 in. length of straight wire formed at each end into a small hook. A series of gauge marks were scribed along the length of the wire by means of a tungsten carbide knife mounted in a jig. The length between the gauge marks (about 0.3 in.) were measured to within ± 0.0001 in. on a travelling microscope. At selected intervals during a run, the apparatus was cooled to room temperature, the specimen removed and measurements made of the length changes in the individual gauge lengths.

The general arrangements of the electron-bombardment apparatus is shown in Fig. 1. The wire specimen was suspended vertically at the center of a series of tungsten filament wires lying parallel to the specimen. The lower end of the specimen, which carried a small weight of the same material, was shielded from the electron stream by a Vycor* sheet. The array was contained in a Vycor chamber which could be evacuated to a pressure of better than 10^{-5} mm Hg. The filaments were held at zero potential and the specimen at 2–3 kV positive.

The temperature of the specimen was controlled by varying the electrostatic potential between the specimen and the filaments and the temperature of the filaments themselves. By adjusting the geometry of the filament wires, a central length of the specimen of at least 1.5 in. could be maintained at a constant temperature. A Leeds-Northrup optical pyrometer focused on the wire through the wall of the Vycor chamber was used to measure the specimen temperature.

EXPERIMENTAL RESULTS

The results of initial experiments indicated that satisfactory creep rates could be obtained at 2250°C. However, annealing an unloaded specimen at 2000°C for a minimum of 12 h was found to be necessary if stable behaviour were to result in subsequent creep experiments at the higher temperature. During this annealing period at 2000°C, both recrystallization and grain growth occurred. Most of the grain growth took place during the first few hours, but stable creep behaviour occurred only after the prolonged annealing. The grain boundaries developed in the form of the bamboo structure referred to earlier; this structure has been reported for all metals so far studied by the wire method. An example of bamboo structure in the niobium wire is shown in Fig. 2. The length of the annealed grains corresponded to a mean grain size of some 1.2 mm, in keeping with the grain growth characteristics of niobium reported by BEGLEY¹⁵. There was no measurable change in the recrystallized grain size during the subsequent creep experiments at the higher temperature.

Fig. 3 shows the creep-strain as a function of time for experiments at 2250°C and added loads of zero to 1.5 g. The wires used in each of these experiments were annealed previously under zero added load for 12–14 h at 2000°C in the electron-bombardment furnace. Attempts to simplify the experimental procedure by annealing loaded wires for this length of time were unsuccessful as considerable grain-boundary offsetting occurred which invalidated the creep-strain measurements. After a prior annealing treatment, grain-boundary offsetting still took place but much less frequently. The solid curves in Fig. 3 represent creep-strain measurements from gauge sections in

* Vycor is a transparent refractory consisting almost entirely of fused silica; it contains 96% SiO₂ and 3% B₂O₃. Its properties closely resemble those of fused quartz.

which no grain boundary offsetting was observed. In these sections, the strain rate at a given load decreased initially for a period of 5–6 h and then became constant. The magnitude of the strain rate decreased as the load was decreased. However, even



Fig. 2. Example of "bamboo" grain-structure and offsetting developed in niobium wire at 2250°C. ($\times 20$)

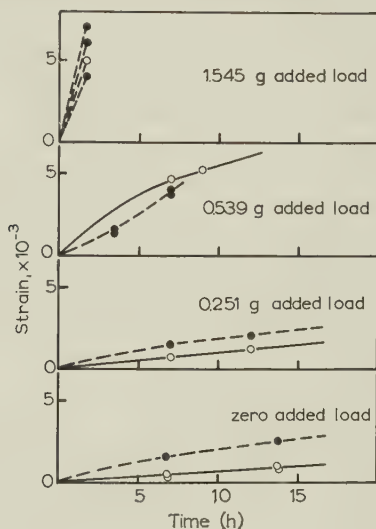


Fig. 3. Effect of applied stress on strain-rate for 0.025 in. diameter niobium wire at 2250°C.



Fig. 4. Example of gross offsetting developed in niobium wire at 2250°C. ($\times 20$)

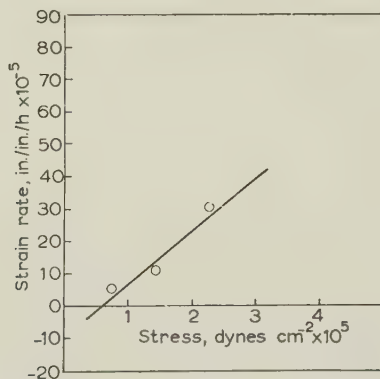


Fig. 5. Strain-rate as a function of applied stress for 0.025 in. diameter niobium wire at 2250°C.

at zero added load there was still sufficient stress from the weight of the specimen alone to prevent the strain rate from becoming negative. The dotted curves show the greater and more erratic deformation found to be associated with the presence of

offsetting. Examples of offset boundaries are shown in the micrographs in Figs. 2 and 4.

A plot of the constant strain rate against the applied stress acting on the gauge section is shown in Fig. 5. The specimen loaded to 1.5 g fractured within a few hours of the start of the creep experiment and constant strain rate conditions were not attained. Accordingly, results for this applied stress are not included in Fig. 5. From the graph, the applied stress that would just balance the surface contractual force is $0.6 \cdot 10^5$ dynes cm^{-2} .

After each experiment, the dihedral angles of the grain boundary grooves formed by thermal etching were measured by a reflected light method similar to that of GREENOUGH AND KING¹⁶. The specimen was held in a goniometer secured to the stage of a metallurgical microscope. The goniometer was adjusted so that the light beam from the microscope objective could be focused on a given grain boundary and the specimen could be rotated in a plane perpendicular to the boundary. By measuring the angle of rotation between reflections of maximum brightness from each side of the boundary groove, the angle of the groove could be determined. The mean boundary dihedral-angle determined for niobium after the experiments at 2250°C was 159.4 degrees. This value was obtained from measurements on a total of some 70 boundaries. Using eqn. (2) the mean grain boundary energy at this temperature was computed to be 0.36 of the surface energy.

From this ratio and the average length of the recrystallized grains, the surface energy of solid niobium at 2250°C was calculated from eqn. (1) as 2100 ergs cm^{-2} . It is considered that this value is accurate to within $\pm 5\%$.

It is of interest to consider the mechanism of deformation in the niobium wires which did not exhibit grain-boundary offsetting. For the small creep strains observed in the experiments, the strain rate should be constant with time if deformation were taking place by the NABARRO-HERRING self-diffusion mechanism¹². Although the strain rate decreased with time during the initial stage of deformation, the fact that subsequently the strain rate remained constant at a value proportional to the applied stress indicates that self-diffusion is probably the controlling mechanism. Similar results have been reported for nickel¹² from measurements of surface energy by the wire method.

DISCUSSION

In order to compare the surface energy obtained experimentally for niobium at 2250°C with calculated values, the experimental value must be adjusted to give the surface energy of the solid metal at the melting point. Although the temperature dependence of the surface energy was not measured, a reasonable value based on the published data for solid metals is 0.5 ergs cm^{-2} deg^{-1} . Assuming such a temperature dependence, the value of the surface energy of solid niobium at the melting temperature (2468°C) is 2000 ergs cm^{-2} . This compares favorably with the theoretical value of 2030 ergs cm^{-2} estimated by TAYLOR⁴ for the surface energy of liquid niobium at the melting temperature. It is to be expected¹⁷ that the value for the liquid would be lower than that for the solid. However, within the probable limits of accuracy, there is no discrepancy between the measured and estimated values for niobium.

In the case of the refractory metals, and also for many other metals, there are insufficient physical data available to permit the useful application of phenomeno-

logical theories of surface energy. For example, ZADUMKIN's successive attempts^{18,19} to compute the surface energies of several refractory metals have given widely different values. However, a number of reasonable correlations appear to exist between the surface energies and other physical properties of the liquid metals. It has been shown by TAYLOR⁴ and confirmed by SIUTA AND BALICKI⁵ that several of these correlations

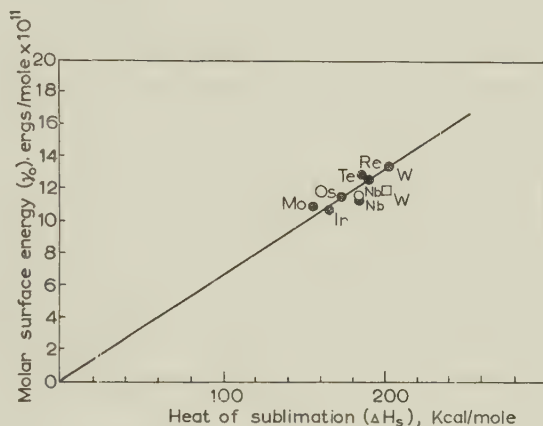


Fig. 6. Relationship between molar surface energy and heat of sublimation: ●, from estimated γ_L values of TAYLOR; □, from experimental γ_L value of CALVERLEY; ○, from experimental γ_s value of present work; —, TAYLOR relationship.

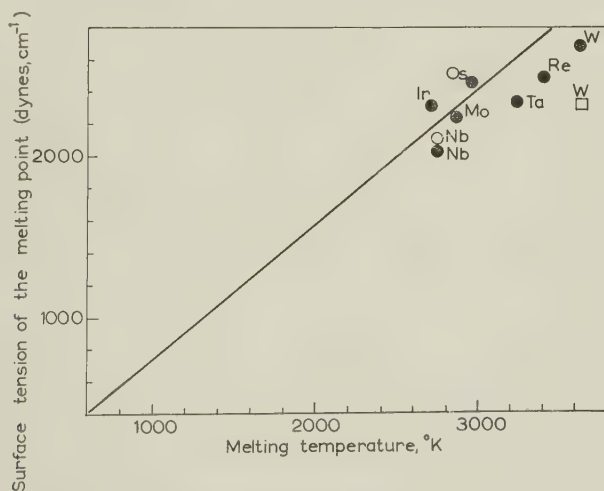


Fig. 7. Relationship between the surface tension and the melting temperature: ●, γ_L values, estimated (TAYLOR); □, γ_L value, experimental (CALVERLEY); ○, γ_s value (present work); —, SIUTA-BALICKI relationship.

are sufficiently exact to yield surface energy values which are accurate to better than $\pm 10\%$. In particular, there is a close correlation between the total molar surface energy and the heat of sublimation. This correlation has justification theoretically from the work of SKAPSKI²⁰.

There are insufficient experimental measurements to attempt any such correlations

for the surface energy of solid metals. However, the difference between the values for the solid and liquid states at the melting point is known to be small. Although the difference increases as the melting point increases, the difference appears to be only some 200 ergs cm^{-2} even with the highest melting metal for which measurements are available¹⁷. Under these circumstances, a correlation which provides an estimate of the surface tension of a liquid metal would also be of assistance in providing an estimate for the solid metal. The best values estimated by TAYLOR for the surface energies of the liquid refractory metals are shown in Fig. 6 plotted in the form of a graph of total molar surface energy against the heat of sublimation. The corresponding values computed from the available measured surface tensions, those for tungsten⁶ and niobium (present work) are also included in the figure. The straight line relationship established by TAYLOR is in quite good agreement with these two values. This agreement indicates that the TAYLOR relationship does provide a way of obtaining meaningful estimates of the surface tension of refractory metals.

SIUTA AND BALICKI⁵ suggested that a simpler correlation exists: that between the surface tension of metals and their melting temperatures. Their suggested correlation is shown in Fig. 7 together with TAYLOR's values for the refractory metals and the experimental values for tungsten and niobium. It is apparent that the SIUTA AND BALICKI correlation is too inaccurate to be useful in estimating surface tension data.

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A STUDY OF METAL IGNITIONS

I. THE SPONTANEOUS IGNITION OF TITANIUM*

F. E. LITTMAN, F. M. CHURCH AND E. M. KINDERMAN

Stanford Research Institute, Menlo Park, Calif. (U.S.A.)

(Received June 23rd, 1961)

SUMMARY

Spontaneous ignition of massive shapes of titanium can occur at room temperature when a fresh, oxide-free metal surface is exposed to oxygen under pressure. Such a surface can be produced by the rupture of a titanium specimen under tension. If these surfaces are exposed to oxygen pressure in excess of 350 p.s.i.g. spontaneous ignition of the sample occurs. With dilute oxygen, using helium or steam as a diluent, higher pressures are required for ignition.

Spontaneous ignition at various concentrations of oxygen was investigated and the effect of temperature on ignition limits was also determined. The hypothesis is suggested that only those metals whose oxides are soluble in the metal will ignite spontaneously and ignition will occur only if the initial reaction is vigorous enough to raise the surface temperature to the melting point of the metal or an eutectic.

INTRODUCTION

Spontaneous ignition of massive titanium was investigated because of concern over inexplicable failures of titanium parts used in test loops in the Homogeneous Reactor Program at Oak Ridge^{1,2}. The damage had the appearance of a burn, and metallographic examination suggested that the α - β transformation temperature (850°C) had been exceeded. The presence of titanium oxide further substantiated the suspicion that the failures were due to a spontaneous ignition of the metal in contact with either hot aqueous solutions or the atmosphere above it, consisting mostly of oxygen under pressure.

Since these reactions occurred spontaneously and appeared to be self-sustaining, they constituted a considerable potential hazard. A project was therefore initiated at Stanford Research Institute to answer the following questions: (1) How are such processes initiated and (2) once initiated, how are they sustained?

SPONTANEOUS IGNITION OF TITANIUM BARS AND ITS LIMITS

Equipment

Suspecting that ignitions occurred when the protective oxide film normally covering the surface of titanium is disturbed, an apparatus was designed which would make possible exposure of oxide-free surfaces to various environments.

A stainless steel high pressure vessel was equipped with a sliding bar, which was in

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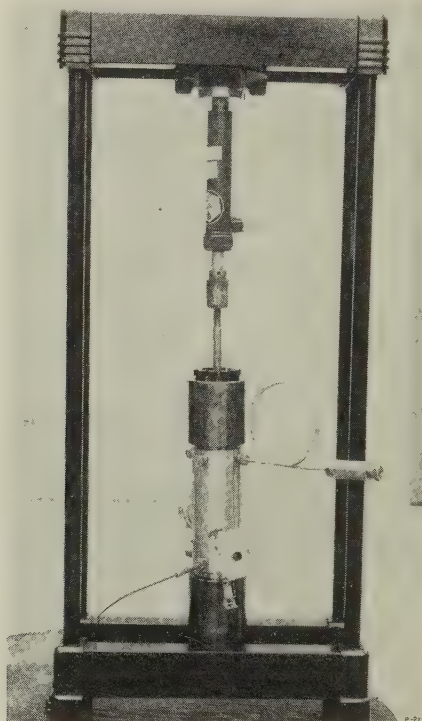


Fig. 1. Reactor assembly.

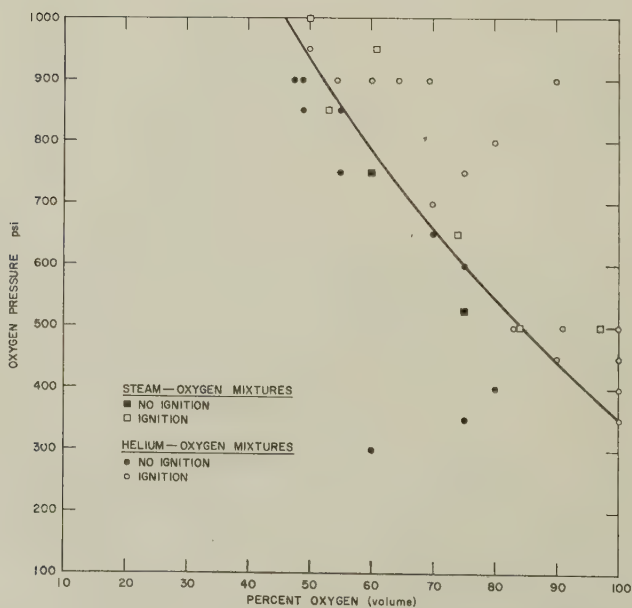


Fig. 2. Reactions of titanium with helium-oxygen and steam-oxygen mixtures. Static tests.

turn connected to a hydraulic ram. Titanium bars, fabricated in the shape of a tensile test specimen, were connected to the sliding bar and broken in tension, thus exposing a fresh surface to the atmosphere. The composition and pressure of the atmosphere surrounding the sample could be varied over wide limits. This equipment is shown in Fig. 1.

Static tests

The procedure used consisted of placing a sample in the reactor, securing the reactor in the steel frame located in an explosion test pit, and pressurizing to the desired pressures. When proper conditions were attained, the sample was broken in tension by the hydraulic pull-ram. The occurrence of an ignition reaction was indicated by a sudden decrease of the gas pressure. The reactor was then vented and opened up for visual inspection of the contents.

The lower ignition limits were established by breaking a series of titanium rods. The pressure for a given oxygen and diluent composition was increased from run to run, until ignition occurred. Sometimes "initial" ignition was noted: that is, the test sample would show burned spots, usually on the edges of the fresh surface, but the ignition did not propagate. The "initial" ignition results were observed under conditions close to the borderline shown in Fig. 2. The results of tests with helium-oxygen mixtures are shown in Table I. Table II shows results obtained under otherwise similar conditions, but using 1/2-in. strips of 12-mil titanium foil in place of the 1/4-in. rod. A third set of results is shown in Table III, where steam was used as a diluent in place of helium.

All of these data are shown graphically in Fig. 2. The line drawn through these points indicates the boundary between the go and no-go regions. There seems to be no significant difference between the behavior of titanium foil and rod, nor between helium and steam as a diluent.

Most of the samples of titanium used in the static experiments consisted of 5-in. lengths of 1/4-in.-diameter rod, reduced to a 1/8-in.-diameter cross section near the middle, with a 1/2-in. taper. Several runs were made with differently shaped specimens. Some rods were reduced to 1/8 and 1/16 in., respectively, by a square-cut groove

TABLE I
REACTIONS OF 1/4-in. TITANIUM ROD WITH HELIUM-OXYGEN MIXTURES
(Static conditions)

P_{O_2} (p.s.i.g.)	P_{He} (p.s.i.g.)	P_{total} (p.s.i.g.)	O_2 (%)	Ignition
300	200	500	60	no
400	100	500	80	no
300	100	400	75	no
400	—	400	100	yes
500	100	600	83	initial
500	50	550	91	initial
900	100	1000	90	yes
800	200	1000	80	yes
700	300	1000	70	initial
750	250	1000	75	(1/2 only)
950	950	1900	50	yes
900	1000	1900	47.5	no

TABLE II
REACTIONS OF 0.012-in. TITANIUM FOIL WITH HELIUM-OXYGEN MIXTURES

P_{O_2} (p.s.i.g.)	P_{He} (p.s.i.g.)	P_{total} (p.s.i.g.)	O_2 (%)	Ignition
500	—	500	100	yes
450	—	450	100	yes
350	—	350	100	no
350	—	350	100	yes
900	950	1850	48.5	no
900	750	1650	54.5	yes
900	600	1500	60.0	yes
900	400	1300	69.0	yes
900	500	1400	64.0	yes
700	300	1000	70	yes
450	50	500	90	yes
850	900	1750	48.5	no
850	700	1550	55.0	no
650	280	930	70	no
600	200	800	75	no
500	100	600	83.5	no

TABLE III
IGNITION IN PRESENCE OF STEAM

P_{O_2} (p.s.i.g.)	P_{steam} (p.s.i.g.)	P_{total} (p.s.i.g.)	O_2 (%)	Temperature (°C)	Ignition
500	15	515	97	100	initial
500	100	600	83	165	initial
650	225	875	74	200	initial
950	600	1550	61	250	yes
1000	1000	2000	50	285	yes
525	175	700	75	188	no
750	500	1250	60	241	no
850	750	1600	53	275	yes

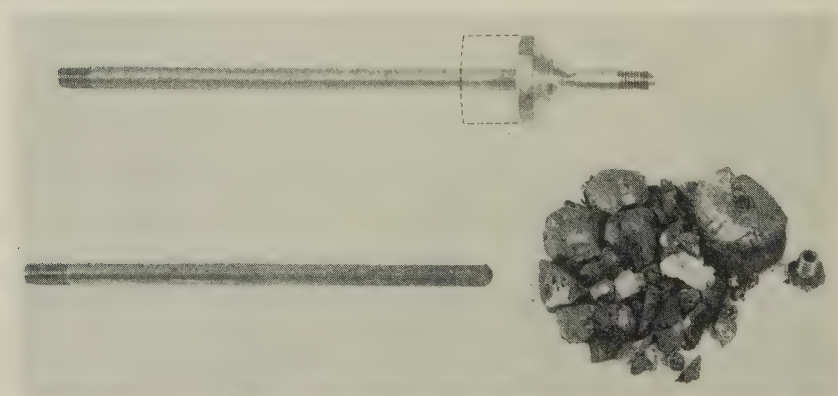


Fig. 3. Ignition of titanium poppet.

near the center, resulting in a very abrupt change in diameter. Another sample was machined from 1-in. round stock to resemble the poppet in the valves mentioned in

ORNL Report No. 56-8-214. Its cylindrical section was about 1 in. long, with a 60° taper coming to a 1/8-in. point attached to a 1/4-in. rod. (See Fig. 3: the burned sample had a longer cylindrical section.) This sample weighed 72 g. In still other runs, 1/2-in. strips of 0.012-in. titanium foil were used. All of these samples ignited readily upon breaking and were completely consumed or melted, even though in the case of the large poppet only 25% of the amount of oxygen required for complete oxidation was present. These tests indicate that, in the presence of oxygen at the necessary pressures, exposure of a very small fresh area can result in a self-sustaining reaction.

Several different titanium alloys were used, such as A-55, A-110 AT, and 6 Al-4V. The results obtained with these samples did not differ within the limits of experimental error, which are of the order of ± 25 p.s.i.g.

The above experiments were carried out at room temperature. The effect of elevated temperature on ignition conditions was also examined. The pressure vessel

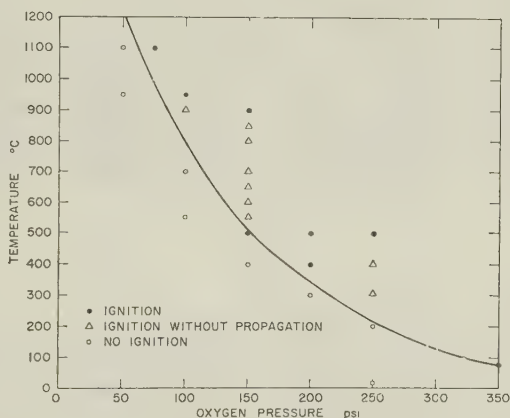


Fig. 4. Effect of initial temperature on ignition of titanium rods.

was modified by insulating the pull-ram electrically from the body of the bomb. This was done by enlarging the guide hole of the rod connecting the pull-ram and the sample, filling it with a reinforced Epoxy resin and redrilling to size. With this insulating sleeve between the extension rod and the body of the bomb, a heavy AC current could be passed through the mounted sample. The temperature of the narrowest portion of the sample as a function of the applied voltage was determined with an embedded platinum, platinum-10% rhodium thermocouple.

In the actual runs the temperature was not measured, but was estimated from the applied voltage. This procedure resulted in an uncertainty of about $\pm 5\%$ in the temperature assumed. The sample was heated in the presence of oxygen until it reached the desired temperature (10 min). The current was then shut off and the sample was broken in tension. The results are tabulated in Table IV and shown in Fig. 4. The minimum oxygen pressure for spontaneous ignition upon rupture of the sample drops from 350 p.s.i.g. at room temperature to 210 p.s.i.g. at 300°C, to 150 p.s.i.g. at 500°C, and to 75 p.s.i.g. at 1000°C. The wide range of "ignition but no propagation" indicated in Table IV seems to contradict our previous experience,

TABLE IV
TEMPERATURE DEPENDENCE OF IGNITION TEMPERATURE OF TITANIUM

P_{O_2} (p.s.i.g.)	Temperature (°C)	Ignition
250	500	Yes
250	400	Yes
250	300	Yes
250	300	Yes
250	200	No
250	room	No
200	500	Yes
200	400	Yes
200	300	No
150	m.p.	Yes
150	900	Yes
150	850	Yes
150	800	Yes
150	700	Yes
150	650	Yes
150	600	Yes
150	550	Yes
150	500	Yes
150	500	Yes
150	400	No
100	950	Yes
100	900	Yes
100	700	No
100	500	No
75	1100	Yes
50	1100	No
50	950	No

which indicated that propagation occurred readily once the sample was ignited. This situation is, however, probably due only to a peculiarity of our experimental arrangement: since the sample was heated by passing a current through it, only the narrowest portion was at the predetermined temperature. The steep temperature gradient from the narrow section to the end of the rod may have resulted in effective quenching of the ignition. This view is supported by the fact that propagation of the ignited sample did occur more regularly when a sample with a longer conical section was used.

To gain a more detailed understanding of the reaction taking place at the freshly formed titanium surface, the reaction was recorded by a Fastax camera, at a framing rate of about 6000 frames per second. The burning of the rod provided sufficient illumination to expose the film. Synchronization was achieved by prestressing the sample to the point where the next stroke of the hydraulic pump would cause rupture. The camera was started, and the sample was broken 0.2–0.4 sec later. This procedure allowed the camera to come up to speed and left 0.3–0.5 sec for recording the ignition.

Selected frames are shown in Figs. 5 and 6. The first frame of Fig. 5 clearly shows the flash which enveloped the fresh surface an instant after the rupture. A puff of

Time
from
rupture
(msec)

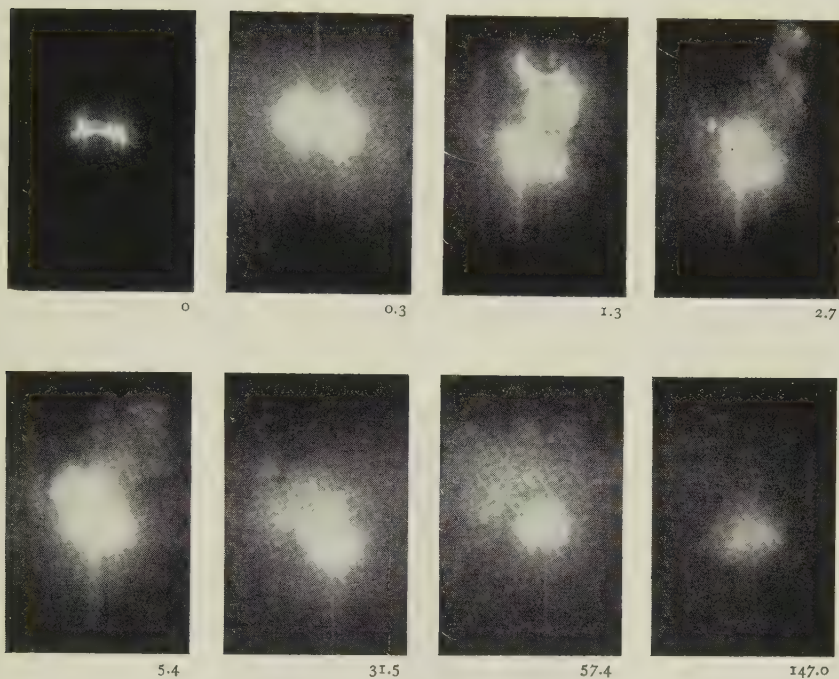


Fig. 5. Ignition of titanium rod.

Time
from
rupture
(msec)

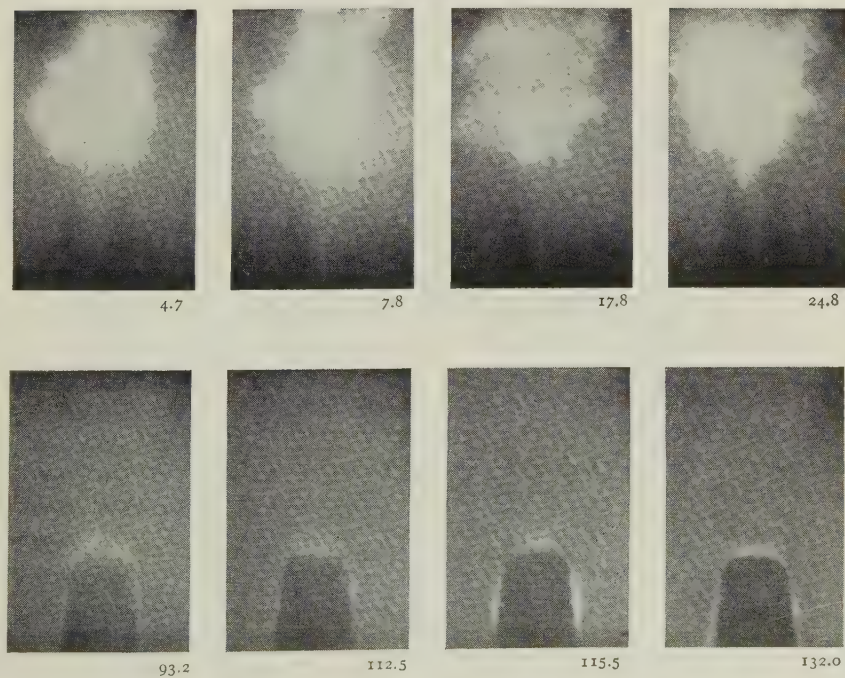


Fig. 6. Ignition of titanium rod.

white smoke appears and the rod begins to burn rather quietly, without much sparking, melting down as time goes on (see last three frames of Fig. 6).

IGNITION LIMITS OF TITANIUM SHEET UNDER DYNAMIC CONDITIONS

The reactor was equipped with a special head to hold down a titanium rupture disk, which was broken by a spring-loaded plunger. Either water or steam could be selected as the material initially in contact with the disk, depending upon the orientation of the reactor. A very high degree of turbulence existed as the contents of the reactor were discharged through the break in the rupture disk. The thickness of the disks varied from 4 to 12 mils. Fig. 7 shows the arrangement with the rupture disk facing downward.

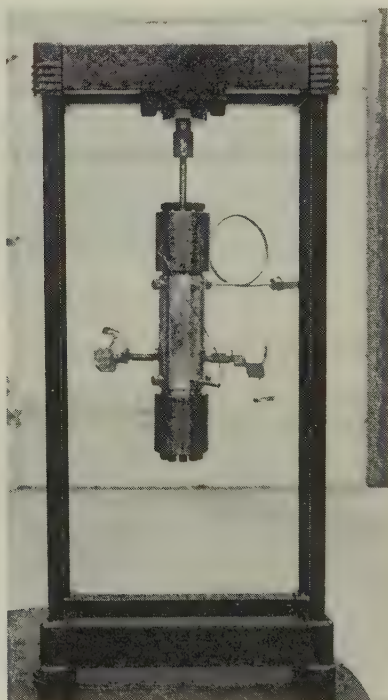


Fig. 7. Reactor assembly for use with rupture disk.

The relationship between oxygen pressure and concentration necessary to produce autoignition of a titanium specimen under dynamic conditions of gas flow was determined in a series of runs in which the oxygen concentration at a given total pressure of oxygen and diluent was increased until ignition occurred. The results, given in Fig. 8 and Table V, show that ignition occurs much more readily under dynamic than under static conditions: pure oxygen at 50 p.s.i.g. pressure, streaming past a fresh surface, produced autoignition. The ignition limits are much lower throughout the whole range of oxygen concentrations. Fig. 9 shows the appearance of a reacted disk.

A number of runs were made with the rupture disks facing down, so that the disk

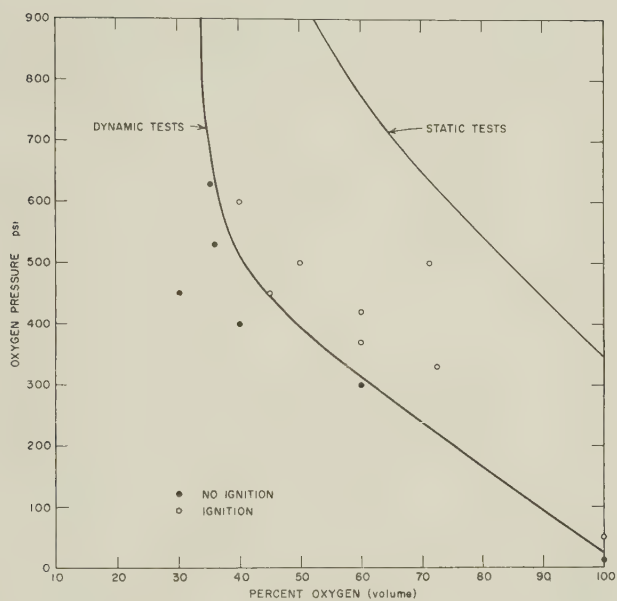


Fig. 8. Reactions of titanium with helium-oxygen mixtures. Dynamic tests.

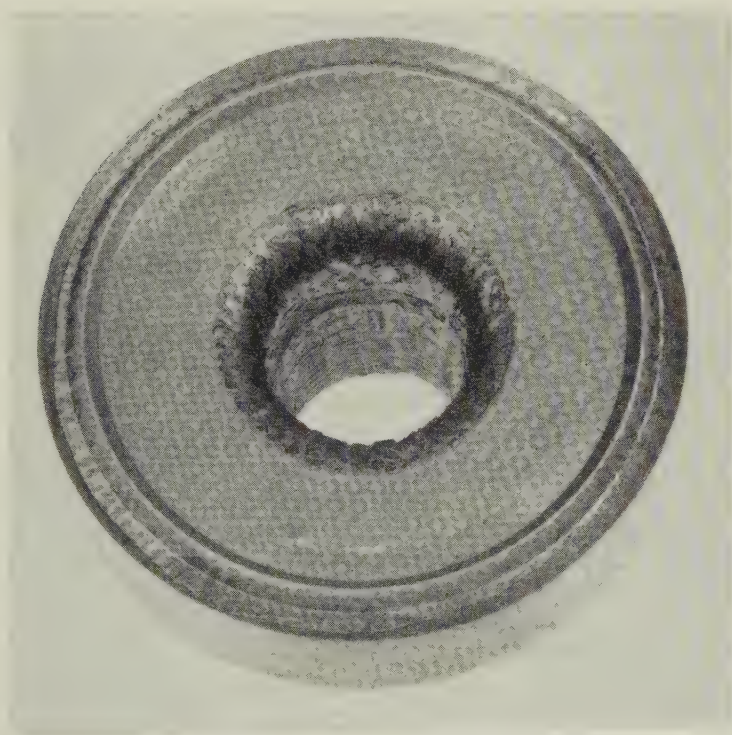


Fig. 9. Rupture disk after reaction.

TABLE V

REACTIONS OF TITANIUM WITH HELIUM-OXYGEN MIXTURES UNDER DYNAMIC CONDITIONS

Foil thickness (in.)	P_{O_2} (p.s.i.g.)	P_{He} (p.s.i.g.)	P_{total} (p.s.i.g.)	O_2 (%)	Ignition
0.003	350	—	350	100	yes
0.003	300	—	300	100	yes
0.003	250	—	250	100	yes
0.003	200	—	200	100	yes
0.003	150	—	150	100	yes
0.003	100	—	100	100	yes
0.003	50	—	50	100	yes
0.003	10	—	10	100	no
0.012	50	—	50	100	yes
0.008	500	500	1000	50	yes
0.008	400	600	1000	40	no
0.008	450	550	1000	45	yes
0.008	420	280	700	60	yes
0.008	370	250	620	60	yes
0.008	340	130	470	72.5	yes
0.008	300	200	500	60	no
0.012	450	1050	1500	30	no
0.012	450	1050	1500	30	no
0.012	540	960	1500	36	no
0.012	600	900	1500	40	yes
0.012	630	1170	1800	35	no
0.012	500	200	700	71.5	yes

was originally in contact with oxygenated water. The concentration of oxygen in water was varied by increasing the oxygen pressure above the water up to 1850 p.s.i.g., which resulted in concentrations up to 7200 p.p.m. dissolved oxygen. In no case was there any indication of reaction of the oxygenated water with titanium even under streaming conditions.

PROPAGATION STUDIES

To start a self-sustaining reaction between titanium and oxygen, a very rapid rate of reaction has to be attained to raise the temperature of the specimen enough to continue the burning. If the initial energy is supplied from exterior sources, milder conditions should be adequate to maintain the reaction.

A different reactor was built for these experiments. It consisted of a cylindrical body 4 in. in diameter and 8 in. long, with a standard head and closure. Two insulated lead-ins were provided in the head. The sample was fastened to these leads. Power for heating the sample was furnished by an a.c. welding transformer capable of delivering 175 amp at 20 V. A 1/4-in. high pressure line and a valve completed the setup. The samples consisted of 1/2-in. strips of titanium foil 0.012 in. thick and about 6 in. long, bent into a U shape and notched at one end.

For the first run the reactor was filled with oxygen at 1 atmosphere pressure and the reaction was initiated by passing a current through the notched sample until it melted (about 5 sec). The reaction continued, consuming the whole sample. Air was used in another run; under these conditions there was no propagation, the reaction

ceasing as soon as the sample melted and broke the circuit. The minimum oxygen concentration necessary at other pressures was determined similarly. The results are shown in Table VI and Fig. 10. The curve in the figure is markedly to the left of the

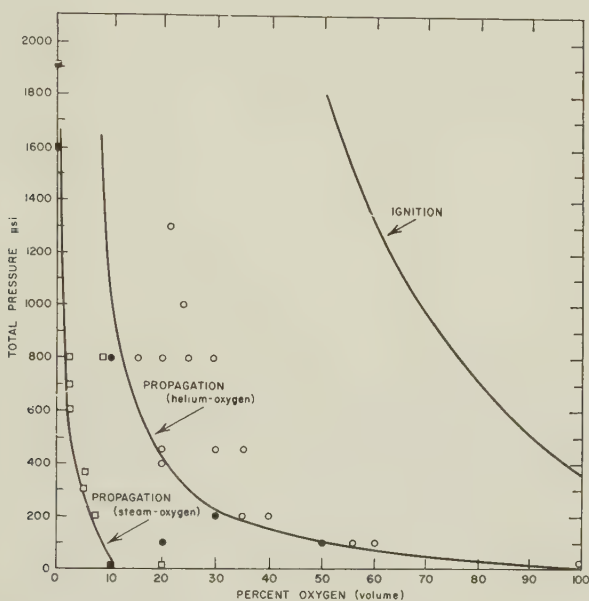


Fig. 10. Ignition propagation in helium-oxygen and steam-oxygen mixtures.

TABLE VI

PROPAGATION OF REACTION OF TITANIUM WITH HELIUM-OXYGEN MIXTURES

O_2 (%)	He (%)	P_{total} (p.s.i.g.)	Ignition
100	—	0	yes
20	(air)	0	no
20	80	100	no
50	50	100	no
60	40	100	yes
55	45	100	yes
30	70	200	no
40	60	200	yes
35	65	200	yes
20	80	400	initial
20	80	450	yes
35	65	450	yes
30	70	450	yes
10	90	800	no
15	85	800	no
20	80	800	initial
25	75	800	initial
30	70	800	yes
25	75	1000	yes
22	78	1300	yes

TABLE VII
PROPAGATION OF REACTION OF TITANIUM WITH STEAM-OXYGEN MIXTURES

O_2 (%)	H_2O (%)	P_{total} (p.s.i.g.)	Ignition
5	95	0	no
10	90	0	yes
20	80	0	yes
7.5	92.5	200	yes
5.0	95	300	yes
5.5	94.5	370	yes
2.5	97.5	600	yes
2.1	97.9	700	yes
20	80	800	yes
10	90	800	yes
2.5	97.5	830	yes
0	100	1600	no
0	100	1900	no

curve delineating the spontaneous ignition limits of titanium in similar mixtures. This indicates that the reaction will continue under much less drastic conditions than were necessary for spontaneous initiation by exposure of a fresh surface.

A similar set of experiments was performed with steam-oxygen mixtures. The pressure vessel was charged with about 100 ml of water, a calculated amount of oxygen was added, and heat was applied until the desired pressure was reached. The reaction was then initiated by passing current through the sample until it melted in the notched area.

The results obtained with steam-oxygen mixtures are quite different from those obtained with helium-oxygen mixtures. As little as 10% oxygen in steam at one atmosphere was enough to sustain the reaction, and at higher pressures less than 5% was needed. Pure steam, however, did not sustain the reaction even at 1900 p.s.i.g. The results are tabulated in Table VII and shown graphically in Fig. 10.

CONCLUSIONS

Some of the limiting conditions for spontaneous ignition of massive shapes of titanium have been defined. From the results presented it appears that relatively massive shapes of titanium will spontaneously ignite if a fresh surface is produced, *e.g.*, by rupturing a sample, in the presence of oxygen under pressure. The mechanism of this reaction is uncertain, but may involve the melting that results from initial reaction. Since the oxide is soluble in the molten metal, no protective surface coating is formed and the reaction becomes self-sustaining. The limiting conditions may be those that generate enough heat during the initial stages of this reaction to melt the surface of the metal.

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A STUDY OF METAL IGNITIONS

II. THE SPONTANEOUS IGNITION OF ZIRCONIUM*

F. E. LITTMAN, F. M. CHURCH AND E. M. KINDERMAN

Stanford Research Institute, Menlo Park, Calif. (U.S.A.)

(Received June 23rd, 1960)

SUMMARY

In continuation of an investigation of the spontaneous ignition of titanium, the behavior of zirconium was determined. It was found that zirconium sheet, varying in thickness from 0.010 to 0.250 in., could be ignited by exposing it rapidly to oxygen under pressure. The ignition limits, in terms of oxygen pressure and concentration, necessary to produce spontaneous ignition, were determined for zirconium and Zircaloy. Ignition resulting from the breaking of 1/4 in. bars (in tension) was also investigated. The ignition limits were of the same order of magnitude, that is about 500 p.s.i.g. of oxygen.

One of the most interesting aspects of these phenomena is the relative unimportance of the protective oxide layer. Where oxide-free samples required a minimum oxygen pressure of about 300 p.s.i.g. for spontaneous ignition, oxidized samples would be ignited with about 450 p.s.i.g. of oxygen. This suggests that under some conditions an oxide layer does not result in a diffusion-controlled mechanism.

INTRODUCTION

Historically, ignition of metals has been associated with the metal in a finely-divided state, and past research^{1,2} has suggested that there is a good probability that all metals become pyrophoric when the ratio of surface-to-volume becomes sufficiently high. However, in some instances of spontaneous ignition of zirconium and titanium, in particular the sudden failure of titanium valves and impellers used in the Homogeneous Reactor Program test, relatively massive shapes of the metal were involved³.

The results of an initial investigation in this field⁴ allowed description of the conditions under which titanium specimens could ignite at room temperature. These conditions appeared to involve a fast, exothermic reaction with oxygen under pressure of a freshly-formed surface unprotected by an oxide film. The fresh surface was formed by rupturing a sample in tension; limiting conditions of oxygen pressure and concentration were defined, and a mechanism postulated which (1) limited the occurrence of a self-sustaining reaction to those metals whose oxides were soluble in the molten metal and (2) required initial conditions sufficiently vigorous to raise the surface temperature of the metal to its melting point.

As a sequel, the present study of the autoignition of zirconium was initiated at Stanford Research Institute by the U.S. Atomic Energy Commission with the aim of

* This work was performed under Contract No. AT(04-3)-115, Project Agreement No. 12 with San Francisco Operations Office, U.S. Atomic Energy Commission.

screwed into the base of the bomb and into one end of the bar. The vessel was then pressurized to the desired degree and the bar broken in tension. A slight modification allowed the samples to be twisted for the break-in-torque experiments.

When sheet samples, enclosed in a glass envelope were used, the direction of travel of the bar was reversed and the envelope was crushed.

For some of the later work a window was cut into the side of the reactor, which is not shown in Fig. 1. A 1/2-in. Pyrex plate was generally used as a closure, although rock salt and quartz windows were also used as the occasion demanded it.

Samples broken in tension

Notched tensile specimens were machined from 1/4-in. zirconium rod by turning a double-truncated cone with the base of 1/4-in. and the top of 1/8-in. diameter. The rods all came from the same ingot and heat, and were machined under identical conditions. They were enclosed in a pressure vessel, surrounded by the desired atmosphere, and broken in tension. The results obtained are shown in Table I. In

TABLE I
IGNITION OF NOTCHED ZIRCONIUM RODS

Oxygen pressure (p.s.i.g.)	Ignition	% Ignition**
500	yes	
600	yes	
600	no	66
600	yes*	
700	yes	
700	yes*	
700	yes	75
700	no	
800	yes	
800	no	50
1000	yes	
1000	yes	
1000	yes	100
1000	yes	

* Ignition, but no propagation, as indicated by burned spots.

** Based on the number of samples igniting $\div$ the number tested.

general, the incidence of ignition increased with increasing oxygen pressure. Compared with similar experiments in which titanium rods were used, the reproducibility was poor. The appearance of a reacted sample is shown in Fig. 2.

The variability of these results was thought to be related to the higher heat conductivity of zirconium. To minimize the effect of the mass of metal, another set of rods was machined to a cylindrical cross section of 1/8-in., instead of the 1/8- to 1/4-in. cone. These were again broken in tension, with the results shown in Table II. The change in the shape of the sample did not result in better reproducibility.

Samples broken in torque

Although the exact reason for the variability of the results discussed in the preceding paragraph was not known, it was suspected that the variable microstructure of the fresh surface was responsible for the lack of reproducibility.

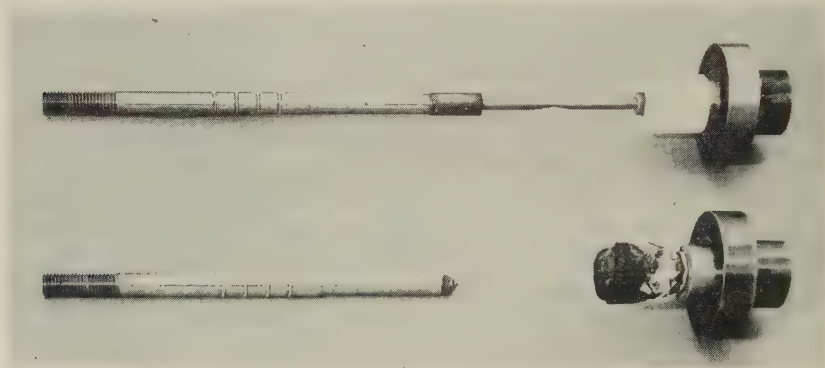


Fig. 2. Ignition of zirconium rod.

TABLE II
IGNITION OF CYLINDRICAL ZIRCONIUM RODS

Oxygen pressure (p.s.i.g.)	Ignition
500	no
600	no
650	yes
650	no
750	no
750	yes
900	yes
900	no
1000	yes
1000	yes

It was suggested⁷ that samples broken in torque might have a smoother, more reproducible surface. Accordingly, the equipment was modified to permit twisting of a slightly stretched bar sample, and a series of tests was made. Breaking in torque did produce a smoother surface than that produced in tension (Figs. 3 and 4). This smoother surface also appeared to be quite reproducible. But, at the same time, no ignition occurred with oxygen pressures up to 2000 p.s.i.g., although samples ruptured in tension ignited regularly with less than half this pressure. It appears, therefore, that the roughness of the surface formed on breaking is of critical importance when working with zirconium bars.

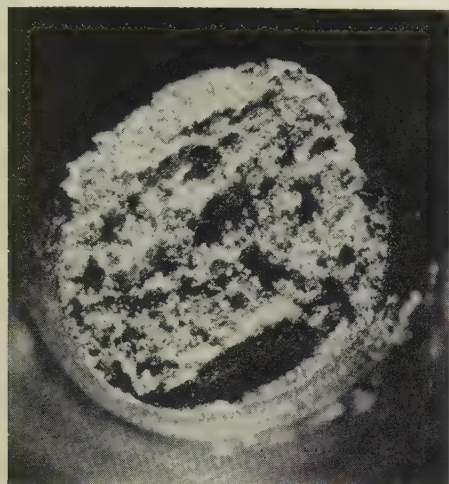


Fig. 3. Surface of rod broken in tension. ($\times 25$)

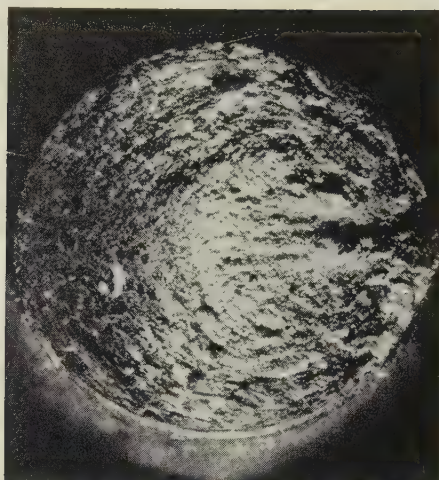


Fig. 4. Surface of rod broken in torque. ($\times 25$)

IGNITION LIMITS OF ZIRCONIUM SHEET

The general technique in working with sheet zirconium was to enclose the sample in a sealed Pyrex tube, flushed with argon. The sheets were about $1/2$ by 3 in. and varied in thickness from 0.010 to 1.250 in. The envelope containing the sheet was then inserted into the high pressure vessel described earlier, surrounded by an atmosphere

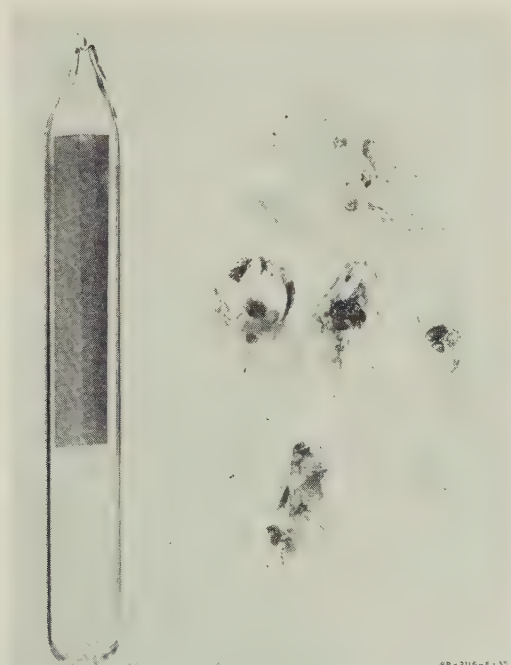


Fig. 5. Zirconium strip before and after reaction.

of the desired oxygen concentration and pressure, and crushed under the hydraulic ram. This provided a means for exposing the sheet very rapidly to oxygen under pressure. Figure 5 shows a strip before and after reaction.

Samples with "clean" surfaces

Since the reaction of "clean" metal represents the simplest case theoretically, and should have the lowest ignition limits, considerable effort was devoted to the preparation of oxide-free surfaces.

Zirconium owes its normal stability to the presence of an inert, adhesive oxide layer, which slows down room-temperature oxidation to a point where it becomes almost unmeasurable. This layer can be removed only in vacuum or in an inert atmosphere. Heating of the zirconium to 800-850°C increases the rate of diffusion of the oxide into the metal until a "clean" surface is produced, provided the pressure in the system is less than 10^{-6} mm Hg⁵.

To achieve such a clean surface on zirconium, a high vacuum system was built which permitted induction heating of a zirconium specimen. It consisted of a Kiney UC-2 forepump, a Consolidated Engineering three-stage fractionating diffusion pump, and the necessary traps and manifolds. The pressures were measured with a Phillips gage, for the range down to 10^{-7} mm Hg, and a Consolidated VG-1A ionization gage with a GIC-110 control unit, capable of measuring pressures to $2 \cdot 10^{-9}$ mm Hg. This system was capable of pumping down to 10^{-8} mm Hg in a few hours.

It was planned to heat a strip of zirconium to 800-900°C at a pressure of the order of 10^{-8} mm Hg, then to seal off the envelope surrounding it, and to transfer the sealed sample to the pressure vessel for ignition tests. Heating the specimen worked out well enough, using a Lepel 2.5-kv induction unit, which made it possible to heat the sample without heating the glass envelope. Upon sealing off the glass tubing, however, the pressure rose to 10^{-4} to 10^{-5} mm Hg owing to out-gassing of the heated section of glass. This pressure was much too high, since calculations indicated that a monolayer of oxide would be formed in less than 5 minutes at 10^{-8} mm Hg. This difficulty was eventually overcome by using a Hoke bellows-type valve, sealed to the glass system using Kovar tubing so that the complete assembly could be transferred to the pressure vessel.

The system was first carefully "flamed" under vacuum to drive out any adsorbed moisture and gases. It was then allowed to cool, and the zirconium sample was heated by induction without heating of the Pyrex glass envelope. To remove the sample from the vacuum line, an elaborate sealing off procedure was worked out which prevented the desorption of additional gases as the glass melted: this was achieved by the use of a high vacuum valve below the seal-off point. The entire assembly was then transferred to the pressure vessel in which the sample in the envelope was surrounded by an appropriate atmosphere and exposed to it by crushing the envelope. It soon appeared that maintaining the sample at the extremely low pressures for the time necessary to accomplish its transfer was not feasible, and the method was modified by introducing purified helium into the system and carrying out this operation in an inert atmosphere rather than in a high vacuum. The helium was purified by passing it over a titanium sponge at 800°C to remove all traces of reactive gases. Using either procedure, a lower ignition limit of 300 p.s.i.g. of oxygen pressure was obtained (Table III).

TABLE III

IGNITION OF OXIDE-FREE ZIRCONIUM SAMPLES IN OXYGEN

Oxygen pressure (p.s.i.g.)	Ignition	Annealing atmosphere
275	No	Argon
275	No	Argon
275	No	Argon
275	No	Helium
275	No	Helium
300	Yes	Helium
275	No	Vacuum
300	Yes	Vacuum

The minimum pressure necessary to produce spontaneous ignition depends on the oxygen concentration. The results of tests using oxygen-helium mixtures indicate that no ignition occurred at oxygen concentrations of less than 70% at total pressures up to 2000 p.s.i.g. (Table IV and Fig. 6).

During the time that the procedure for the preparation of oxide-free samples was being perfected, experiments were conducted with zirconium and Zircaloy-2 samples cleaned by etching. These strips, cut from a single sheet of 0.010-in. zirconium, were etched in a nitric-hydrofluoric acid bath, rinsed with water and acetone, and air-

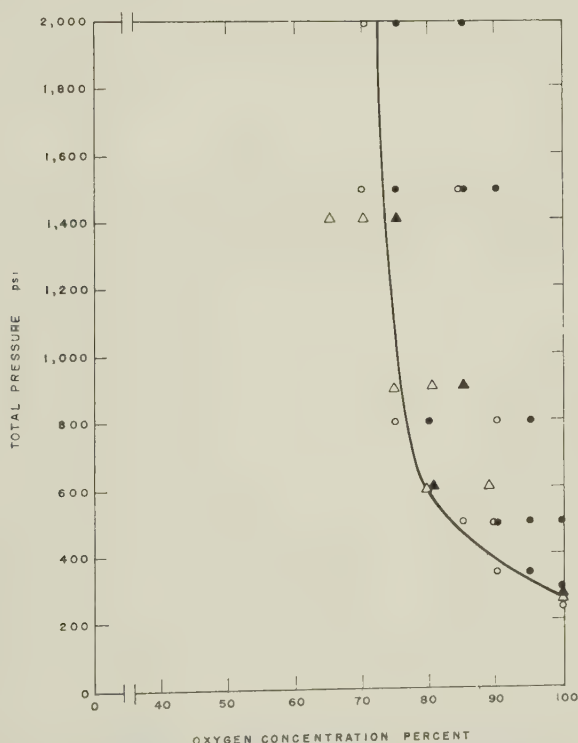


Fig. 6. Ignition limits of etched or annealed zirconium. ●, Etched, ignition; ○, etched, no ignition; ▲, annealed, ignition; △, annealed, no ignition.

TABLE IV

IGNITION OF OXIDE-FREE ZIRCONIUM SAMPLES IN OXYGEN-HELIUM MIXTURES

Oxygen pressure (p.s.i.g.)	Oxygen concentration (%)	Ignition
275	100	No
275	100	No
300	100	Yes
600	80	No
600	90	Yes
600	80	Yes
900	75	No
900	80	No
900	85	Yes
1400	70	No
1400	75	Yes
1400	65	No

dried. They were then sealed into a test tube flushed with argon. Although these samples were clean in any ordinary sense of the word, they were not completely oxide-free, since a thin layer of oxide unquestionably was formed during the drying process when the etched samples were exposed to air.

The results obtained by exposing these samples to oxygen under pressure (Tables

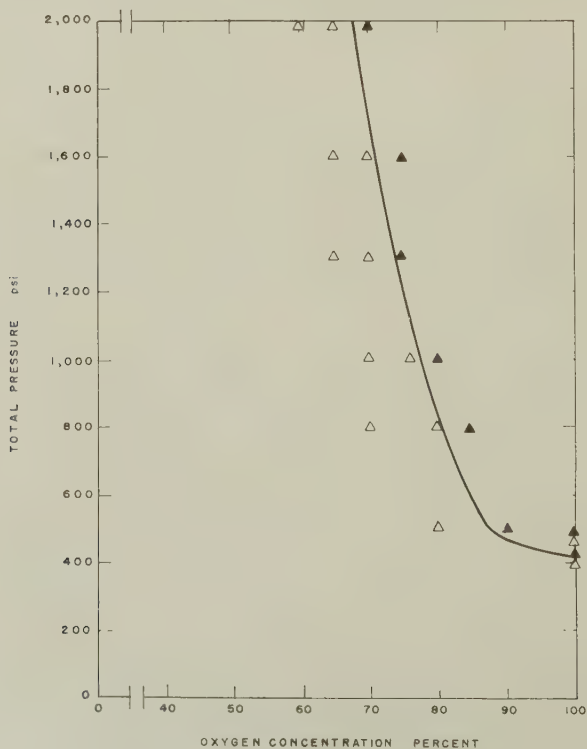


Fig. 7. Ignition limits of etched Zircaloy-2.

TABLE V

IGNITION OF ETCHED ZIRCONIUM SAMPLES IN OXYGEN-HELIUM MIXTURES

<i>Total pressure (p.s.i.g.)</i>	<i>Oxygen concentration (%)</i>	<i>Ignition</i>
450	100	yes
300	100	yes
250	100	no
350	95	yes
350	95	no
500	95	yes
500	90	no
500	90	yes
500	85	no
800	95	yes
800	90	no
800	80	yes
800	75	no
800	75	no
1500	90	yes
1500	85	no
1500	85	yes
1500	75	yes
1500	70	no
1500	70	no
2000	85	yes
2000	80	yes
2000	75	no
2000	70	no

TABLE VI

IGNITION OF ETCHED ZIRCALOY-2 SAMPLES IN OXYGEN-HELIUM MIXTURES

<i>Total pressure (p.s.i.g.)</i>	<i>Oxygen concentration (%)</i>	<i>Ignition</i>
400	100	no
450	100	yes
450	100	no
500	100	yes
500	90	yes
500	80	no
800	70	no
800	80	no
800	85	yes
1000	80	yes
1000	75	no
1000	70	no
1000	75	yes
1300	70	no
1300	65	no
1600	70	no
1600	75	yes
2000	70	yes
2000	65	no
2000	60	no
2000	65	no

V and VI, Figs. 6 and 7) were not only reasonably reproducible, but they were also indistinguishable from the results obtained with oxide-free samples. Figure 9 also contains the points obtained with oxide-free material.

These results were surprising in view of all previous experience, which indicated that an oxide-free surface was necessary for ignition. This disagreement of results was one reason for the mechanism studies described subsequently.

Oxidized, hydrided and carbided samples

When it was found that the thin oxide layer present on etched samples did not have a measurable effect on the minimum oxygen pressure necessary for spontaneous ignition, further tests were conducted with samples having contaminated surfaces. In the first series, zirconium was used in "as-received" condition. No effort was made to clean the surface of fingerprints, etc.; the sheets were relatively clean, however, without any visual indication of an oxide layer. For the second series of tests, zirconium strips were oxidized by heating them in an oxygen atmosphere to

TABLE VII
IGNITION OF "AS-RECEIVED" ZIRCONIUM SAMPLES IN OXYGEN

Oxygen pressure (p.s.i.g.)	Ignition
1000	Yes
750	Yes
500	Yes
500	Yes
450	No
450	No
400	No
350	No

TABLE VIII
IGNITION OF OXIDIZED ZIRCONIUM SAMPLES IN OXYGEN

Oxygen pressure (p.s.i.g.)	Ignition
300	No
350	No
400	Yes
400	Yes
500	Yes

about 600°C for 10 min. A black, coherent oxide coating resulted. These strips, too, were enclosed in a Pyrex envelope and rapidly exposed to oxygen under pressure. As can be seen from Tables VII and VIII, the minimum oxygen pressures required for spontaneous ignition were only slightly higher than for etched or annealed samples — 400–450 p.s.i.g..

To determine whether the ignition resulted from scratching of the surface by glass splinters, a sample of oxidized zirconium was placed in the pressure vessel in the

presence of 1000-p.s.i.g. oxygen and scratched with a steel needle. No ignition resulted.

These results indicate that, at least under the experimental conditions described above, an oxide layer does not provide much protection to zirconium exposed rapidly to oxygen under pressure.

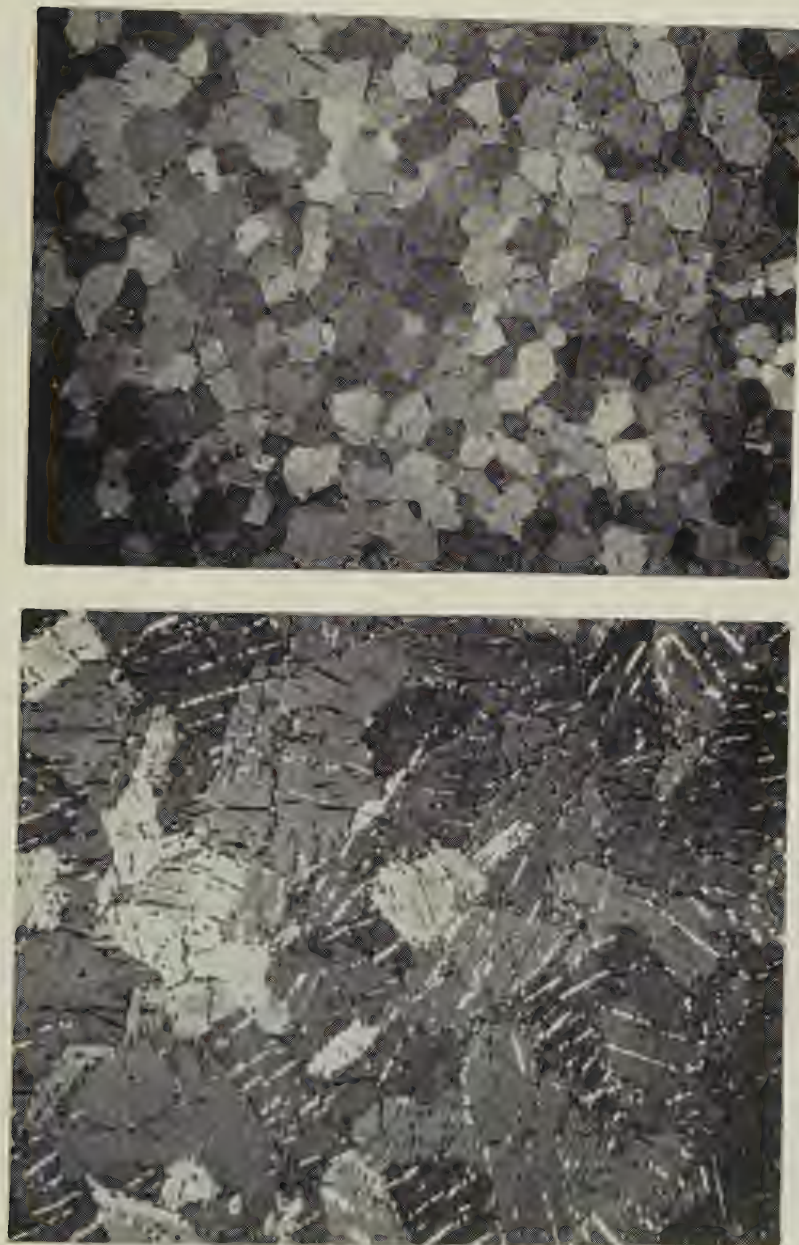


Fig. 8. Photomicrographs of fresh and autoclaved zirconium.

The role of zirconium hydride in the spontaneous ignition of zirconium has long been a subject for conjecture. It has recently been shown that a hydride layer can be formed under certain conditions⁶, and an examination of samples which had been subjected to accelerated aging by autoclaving at 300°C also showed the presence of hydride (Fig. 8). Chemical analysis of these samples gave high but very erratic results, until the surface was abraded. This suggests that here, too, a high concentration of hydride was present near the surface. Thus there appears to be a corrosion-type mechanism which results in a hydride formation on zirconium. To examine the possible importance of such a layer, circular samples, cut from 0.035-in. sheet, were supported on tungsten wires in a Pyrex tube and heated inductively to about 600°C in the presence of 25 mm Hg of hydrogen pressure. The hydrogen was purified by passing it over calcium hydride at 600°C. The samples were hydrided for 10, 30, and 60 min, respectively, and contained, respectively, about 4, 16, and 30% hydride. After hydriding, the tube was evacuated, backfilled with purified helium, sealed off and transferred to the pressure vessel, where the sample was exposed to oxygen under pressure by crushing the envelope. The results, shown in Table IX, indicate that the presence of the hydride does not markedly modify the minimum pressure necessary for spontaneous ignition.

TABLE IX
IGNITION OF HYDRIDE ZIRCONIUM IN OXYGEN

<i>Hydride (%)</i>	<i>Oxygen pressure (p.s.i.g.)</i>	<i>Ignition</i>
4	275	No
4	300	Yes
16	300	Yes
16	275	No
16	275	No
30	300	Yes
30	300	Yes

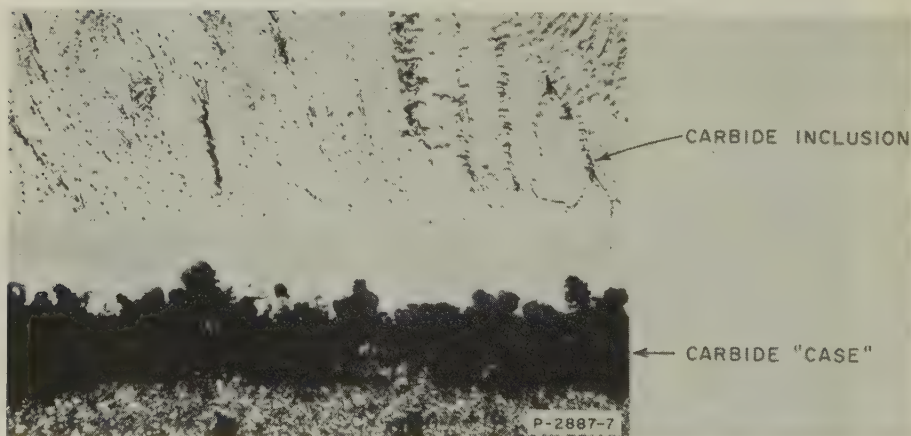


Fig. 9. Photomicrographs of ZrC case on zirconium. ($\times 500$)

Abnormally high carbide content has been reported in conjunction with zirconium which had accidentally ignited³. To examine the relation between carbide and autoignition, zirconium disks were heated in contact with graphite plates to about 540°C for 20–30 min. Metallographic examination of these disks showed a heavy carbide casing, as well as carbide penetration into the center of the metal (Fig. 9). Chemical analysis indicated about 10% carbide content over-all. The carbided disks were then transferred to Pyrex tubes, sealed off, surrounded by oxygen under pressure in the pressure vessel, and the glass envelope broken. The results, shown in Table X, indicate that zirconium carbide is much less susceptible to autoignition than is either the metal or the hydride.

TABLE X
IGNITION OF CARBIDED ZIRCONIUM SAMPLES IN OXYGEN

Oxygen pressure (p.s.i.g.)	Ignition
300	No
450	No
1000	No
1250	No
1500	Yes

STUDIES OF MECHANISM OF IGNITION

Results obtained so far indicate that the ignition of zirconium is dependent on a threshold value of oxygen pressure and concentration. It was postulated that the threshold value was related to surface melting; if the surface did not melt, the resulting oxide film kept the reaction from becoming self-sustaining, *i.e.*, ignition did not occur.

These assumptions could be verified by measuring the instantaneous surface temperature of a zirconium sample immediately before ignition, as a function of oxygen pressure. The temperature at which ignition occurred would be significant in terms of the ignition mechanism. Earlier work, using a high speed movie camera⁴ has indicated that ignition of fresh surfaces took place very rapidly, possibly in less than 100 μ sec. This posed a very difficult instrumental problem of measuring and recording transient temperature changes, which required a good deal of development work. The equipment used consisted of a shock tube and an electronic radiometer.

A shock tube was used because it provided a simple and relatively well understood means for exposing a zirconium sample rapidly to oxygen under pressure, under conditions similar to those of the previously used technique of using glass envelopes, but permitting observation of the sample.

An ideal shock tube is a straight tube divided by a rupture disk into two sections, one containing a gas under high pressure, the other containing a gas at low pressure. When the rupture disk is broken, *e.g.*, by exceeding its rated strength, the driver gas rushes into the test section and compresses the gas before it. The compression wave rapidly (within a few tube diameters) builds into a shock wave which propagates down the test section. The velocity of the shock wave propagation is usually expressed in Mach numbers and depends only on the ratio of driver gas pressure to test gas pressure at the instant of rupture.

The compression of the test gas is essentially adiabatic and results in a temperature rise in the shock-front within the test gas, followed by cooling when the cold driver gas arrives. The conditions prevailing during the first 3 msec in an open-ended shock tube at a point 22 in. downstream of the rupture disk are shown in Fig. 10.

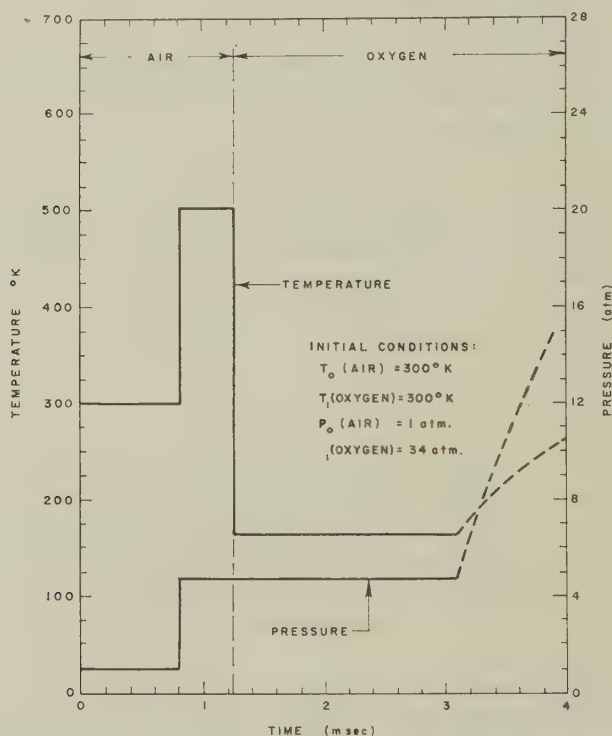


Fig. 10. Schematic diagram of conditions in shock tube.

The shock tube consists essentially of a 24-in. length of 1-in. steel pipe, joined by a special union with a 20-in. length of pipe of the same diameter. The rupture disks are held in the union. The collar near the end of the tube contains a sample holder and a window. The inside bore of the sample holder is the same as that of the pipe. At the upper end of the shock tube is a solenoid valve, connected to a high pressure reservoir.

The samples consisted of strips of zirconium varying in thickness from 0.020 to 0.125 in., about 1/2-in. wide and 3-in. long, mounted coaxially with the pipe.

Just below the union two very small holes permit the ends of the trigger wire, cemented to the rupture disk, to come through the walls of the tube.

In operation, the reservoir was first filled with gas, usually oxygen, at a pressure slightly higher than the bursting pressure of the rupture disk. Using the solenoid valve, the high pressure section was then pressurized until the rupture disk broke, providing a very sudden exposure of the sample to oxygen under pressure. The ensuing reaction was observed through a window at the height of the sample using the Thermodot radiometer.

The radiometer consists of an optical head and a control unit. The optical head is approximately $10\frac{1}{2}$ in. long and $5\frac{1}{2}$ in. in diameter. It is lightweight, portable, and fitted for use with a standard tripod. It contains the radiation collecting optics, infrared detector, mechanical chopper, preamplifier, and a visual sighting mechanism system.

The optical system consists of a collecting mirror and folding mirror designed to have minimum aberration. The sensitivity of the collecting mirror and infrared detector is achromatic over the useful spectral range of the detector. The optical axis of the sighting mechanism is identical to that of the collecting mirror so that the point observed visually is also the point from which thermal radiation is received.

The control unit contains the power supply, wideband amplifier and indicating meter. Output jacks for a recorder and an oscilloscope are provided. In our work it was used in conjunction with a Tektronix 535 oscilloscope.

According to the manufacturer's specifications, the Thermodot has a useful range of 50–5000°C. It is normally operated with a chopper giving an interruption of the light path of 540 counts/sec, or about 1.85 msec per exposure. For faster events the instrument is used without a chopper; in this way it will follow a fluctuating signal. In addition, the manufacturer (Radiation Electronics, Shokie, Ill.) claims a response time of less than $5\text{ }\mu\text{sec}$.

Since the calibration supplied with the instrument does not apply when it is used without the chopper, the Thermodot was calibrated by observing a heated zirconium target for intervals of the order of 1 msec. This was accomplished by passing a variable, heavy current through a zirconium strip contained in a steel tube equipped with a window. An argon atmosphere was maintained in the tube. The temperature of the strip was determined with an optical pyrometer (in the higher ranges) and with the Thermodot itself, operating in its normal, chopped position, for lower temperatures.

Having thus calibrated the target, the response of the Thermodot to a known temperature was determined in the "wideband" position, that is, without the use of the chopper. An information period of approximately 1-msec duration was obtained by interposing a focal plane camera shutter between the target and the Thermodot and "exposing" the Thermodot for $1/1000$ of a second. The values obtained are shown in Table XI.

TABLE XI
CALIBRATION OF THERMODOT

Voltage setting (V)	Target temperature (°C)	Thermodot output (V)
80	280	0.25
90	390	0.50
100	475	1.00
110	560	1.95
120	630	3.2
130	700	5.2
140	765	8.3
150	830	9.5
170	920	14.0
180	990	17.0
190	1060	21.0
200	1140	32.0

These data are shown in Fig. 11. Since the Thermodot responds linearly only to about 1200°C in the "wideband" position, the burning temperature of zirconium can only be measured by using a special aperture, having a transmission of 2%. Using this aperture, an output of about 70 V was obtained, corresponding to 3500 V without the aperture, or about 3000°C. To check this, a zirconium ribbon was burned in a glass tube through which a stream of oxygen was flowing and the temperature ob-

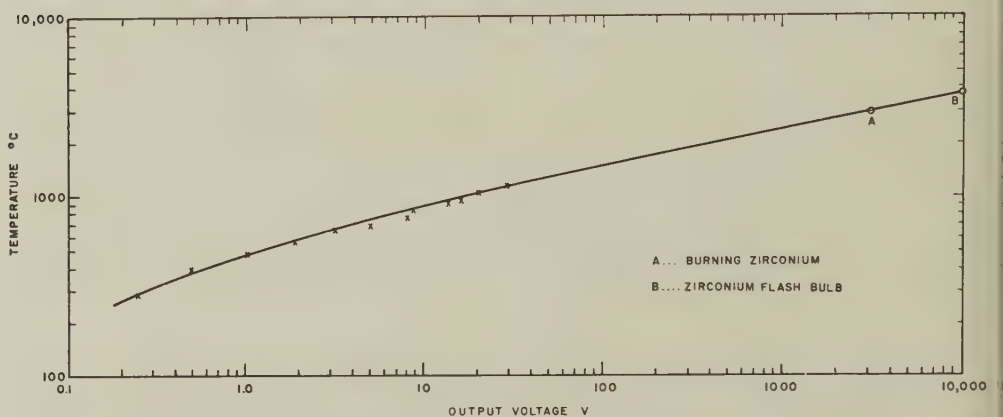


Fig. 11. Calibration of Thermodot radiometer.

served with an optical pyrometer. A reading of $2500^{\circ}\text{C} \pm 10\%$ was obtained. Since the samples normally burn in an atmosphere of oxygen under some pressure, the somewhat higher burning temperature seems quite appropriate.

There remained one more problem before this equipment could be used to follow the initial temperature rise of burning zirconium: the sweep of the oscilloscope had to be synchronized with the onset of the oxidation reaction, presumably triggered by the arrival of the shock wave at the sample. Internal triggering was not successful; neither was an ionization gauge, nor a transducer (the latter was triggered prematurely by transmission of shock in the metal wall). A hot wire trigger, designed to burn out and break when hit by the compressed oxygen, cooled off instead and remained unbroken. The problem was finally solved by cementing a fine (0.0025-in.) insulated copper wire to the rupture disk. The breaking of the wire placed 20 V across the trigger terminals of the oscilloscope and started the sweep. A transducer was placed at the end of the shock tube and the interval between the breaking of the wire and the arrival of the shock wave measured to determine the reproducibility of the wire trigger. It turned out to be reproducible to within $\pm 75 \mu\text{sec}$, which appeared to be adequate for our purposes.

Once the calibration and triggering technicalities were solved, the procedure was fairly simple. A zirconium sample, usually a strip $1/2$ by 3 in. and 0.035 in. thick, was mounted coaxially near the lower, open end of the shocktube. The diaphragm, was put into place, the fine wire, which was cemented to the diaphragm, connected to the triggering circuit of the oscilloscope (Tektronix 535). The Thermodot was then focussed on the sample from a distance of about 18 in. At that distance its field of view is about $1/4$ in. in diameter. The reservoir was pressurized with enough oxygen

to break the rupture disk and the shock tube charged using a solenoid valve. Upon rupture of the disk the sample was thus exposed very rapidly to oxygen under pressure.

A characteristic record trace is shown in Fig. 12. To record both small and large

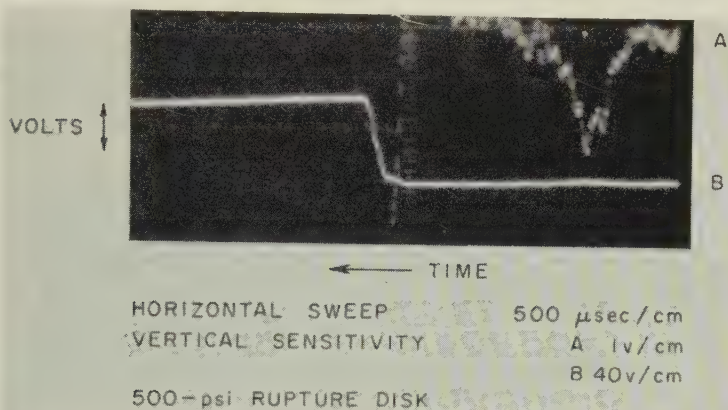


Fig. 12. Surface temperature profile.

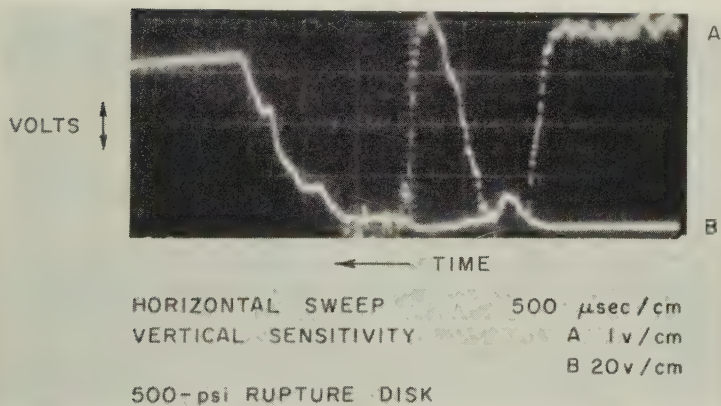


Fig. 13. Surface temperature profile.

temperature changes, the incoming signal was fed into both channels of the oscilloscope, using different vertical sensitivities. The upper, reversed trace indicates a transient temperature rise of about 2 V (about 600°C) about 700 μsec after the bursting of the 500-p.s.i.g. rupture disk. This corresponds roughly to the time of arrival of the shock front, but exceeds the computed shock front temperature. The trace indicates that within another 500 μsec the sample cooled to below starting temperature, in agreement with the temperature profile of the shock wave shown in Fig. 10. Much later, about 2500 μsec after the rupture of the diaphragm, the sample ignited. (The indicated voltage of about 70 V has no meaning, since the amplifier was apparently overloaded by the incoming signal and trimmed in at that level. Separate runs, using a high temperature aperture on the Thermodot, established that

the burning temperature was of the order of 3200–3500°C.) Figure 13 shows a similar, but even more dramatic, course of events.

Similar results were obtained using a 400-p.s.i.g. rupture disk. Using higher pressures (1000 p.s.i.g.) a somewhat different picture presents itself (Fig. 14): the preliminary temperature rise is gone, and ignition results immediately.

Although these traces are characteristic of the behavior of zirconium strips under these conditions, they are not the only patterns found, since ignitions were again quite irreproducible, and occasional runs resulted in no indicated reaction under the

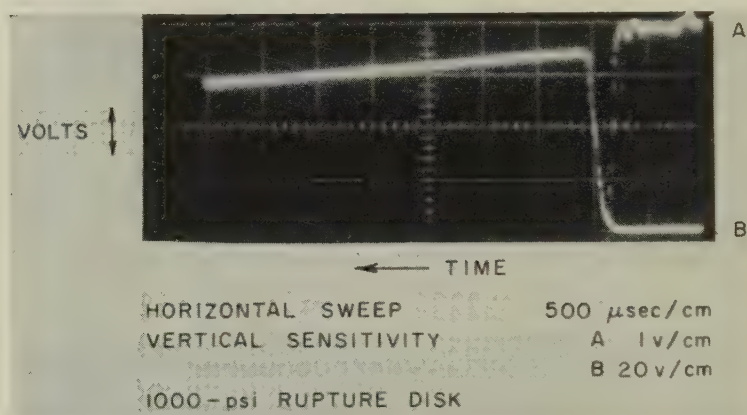


Fig. 14. Surface temperature profile.

same conditions which led to ignition in preceding and subsequent runs.

When an inert gas–argon mixture was used both as a driver and in the test chamber, only a very small temperature increase was shown, indicating that most of the temperature rise seen with oxygen was due to an oxidation reaction, rather than adiabatic heating.

CONCLUSIONS

It has been shown that zirconium and Zircaloy-2 can ignite spontaneously starting at room temperature, if they are rapidly exposed to oxygen under pressure. The limits of oxygen pressure and concentration have been established.

The effect of oxidized, hydrided, and carbided surfaces on spontaneous ignition was evaluated empirically and found to be relatively small. Indeed, the most interesting aspect of the work described in this report is the relative unimportance of the (normally protective) oxide film under these conditions.

Whereas the mechanism of spontaneous ignition of metals with oxide-free surfaces is relatively simple and its characteristics can be explained on the basis of simple kinetic considerations, the ignition mechanism of “protected” metal surfaces is obscure, since models of diffusion-controlled reactions do not agree with the experimental findings described in this report. In particular, diffusion-controlled reactions should be relatively independent of pressure, whereas under the conditions of the experiments reported here pressure appears to be of critical importance.

Attempts to clarify this ignition mechanism by following the first few milliseconds of the reaction with a sensitive, high-speed radiometer indicate that such an approach might provide important information, but within the time limitations of this project no conclusive proof of the mechanism of ignition of oxidized metals was obtained.

Several alternative hypotheses present themselves:

1. Ignition is initiated by the heating due to the adiabatic compression of air in the shock front. This temperature rise results in an increase of the oxidation rate, leading to still higher temperatures, and the reaction becomes self-sustaining; that is, ignition occurs. Since it is known that the rate of diffusion rises rapidly with temperature, this mechanism seems plausible. On the other hand, the experiments with an inert gas (argon) indicated that the original temperature increase is quite small (of the order of 100°C), and this seems insufficient to initiate a self-sustaining reaction.

2. The oxide coating consists of a sub-oxide, which is in equilibrium with the surrounding atmosphere. When this equilibrium is disturbed by rapid pressurization, a change of composition (oxidation) occurs. If this change is rapid enough so that the resulting heat cannot be dissipated, a rapid rise of temperature results, leading to an oxidation of the underlying metal and eventual ignition.

3. The shock wave mechanically produces a defect in the coherent oxide layer—cracking, flaking, or similar phenomena. This is then followed by rapid oxidation of the now unprotected metal surface.

4. A combination of effects may result in a heating of the oxide surface above the transformation temperature of the monoclinic oxide to tetragonal (above 1075°C) resulting in a volume contraction. This in turn exposes a fresh surface to oxygen under pressure, resulting in ignition.

Thus the mechanism of spontaneous ignition of zirconium remains to be determined in future investigations.

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A STUDY OF 2-HYDROXY-3-NAPHTHOIC ACID DERIVATIVES OF BERYLLIUM

R. P. AGARWAL AND R. C. MEHROTRA

Chemical Laboratories, University of Gorakhpur, Gorakhpur, U.P. (India)

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SUMMARY

Potentiometric, conductometric and preparative studies of beryllium 2-hydroxy-3-naphthoate systems indicate the formation of two complexes; the 1:1 complex predominates at a pH of about 5.5 and the 1:2 complex in the ionic form at pH 8-9. In aqueous medium the 1:2 complex is precipitated first by the addition of the potassium salt of the acid to a beryllium sulphate solution, which then changes into the 1:1 complex by the addition of one mole of alkali. In 50% alcoholic medium in which complexes are soluble the formation of 1:1 complex is only indicated in acidic solutions. The stability constants in 50% alcohol of the complexes have been calculated by Bjerrum's method. For comparison, stability constants for salicylate and sulpho-salicylate complexes were also determined under identical conditions. Stability constants k were found to be: $\log k_1 = 11.98$, $\log k_2 = 7.92$; $\log k_1 = 12.45$, $\log k_2 = 8.50$; $\log k_1 = 11.52$, $\log k_2 = 8.90$, respectively for 2-hydroxy-3-naphthoate, salicylate and sulpho-salicylate complexes. Dissociation constants of the acids were determined in 50% alcohol using a hydrogen electrode. New compounds: $\text{BeC}_{11}\text{H}_6\text{O}_3 \cdot 2 \text{H}_2\text{O}$, $\text{H}_2\text{Be}(\text{C}_{11}\text{H}_6\text{O}_3)_2$ and $\text{K}_2\text{Be}(\text{C}_{11}\text{H}_6\text{O}_3)_2$ were isolated.

INTRODUCTION

In a recent communication¹, the complex reactions of beryllium with salicylate ions were reported. In this paper are described recent studies of the corresponding beryllium 2-hydroxy-3-naphthoate systems. It has been shown that the chemical behaviour of these derivatives is almost similar to that of beryllium salicylates, with the difference that beryllium 2-hydroxy-3-naphthoate derivative is precipitated as soon as the potassium salt of the acid is added to an aqueous solution of beryllium sulphate. The following new compounds have been isolated: $\text{BeC}_{11}\text{H}_6\text{O}_3 \cdot 2 \text{H}_2\text{O}$, $\text{H}_2[\text{Be}(\text{C}_{11}\text{H}_6\text{O}_3)_2]$, $\text{K}_2[\text{Be}(\text{C}_{11}\text{H}_6\text{O}_3)_2]$. The system has been further studied by potentiometric and conductometric titrations and the results have been compared with the corresponding beryllium salicylate system.

Since the beryllium 2-hydroxy-3-naphthoate derivatives were insoluble in water, formation constants of the complexes could not be determined in aqueous medium. Attempts have therefore been made to determine the formation constants in 50% alcohol by Bjerrum's method² and the values given in Table I have been found; for comparison, the systems with salicylic and sulpho-salicylic acids have also been studied under identical conditions.

A comparison of the $\bar{n}$ values against $-\log(\text{ligand})$ plots clearly shows an essential

TABLE I
FORMATION CONSTANTS

No.	System	$\log k_1$	$\log k_2$
1	Beryllium 2-hydroxy-3-naphthoate	11.98	7.92
2	Beryllium salicylate	12.45	8.50
3	Beryllium sulphosalicylate	11.52	8.90

difference between the 2-hydroxy-3-naphthoate and salicylate derivatives on the one hand and sulpho-salicylate on the other. The former two curves become almost horizontal at $\bar{n} = 1$ and show the relative higher stabilities of 1:1 complexes. The same is also easily understandable from the values of corresponding spreading factors 53.57, 47.20 and 10.01 calculated from the above data for the 2-hydroxy-3-naphthoate, salicylate and sulpho-salicylate systems respectively in 50% alcohol.

For the above calculations, dissociation constants of the acids were determined in 50% alcohol. The pK_a values determined are given in Table II and compared with those reported earlier in aqueous medium.

TABLE II

Acid	pK_a values in 50% alcohol			Reported pK_a values in water		
	pK_{a1}	pK_{a2}	pK_{a3}	pK_{a1}	pK_{a2}	pK_{a3}
2-hydroxy-3-naphthoic acid	3.65	12.87	—	2.70 ³	—	—
Salicylic acid	3.91	13.13	—	2.99 ⁴	13.12 ⁵	—
Sulpho-salicylic acid	1.60	3.41	12.88	—	2.49 ⁶	11.74 ⁷

EXPERIMENTAL

Solutions of BDH analar beryllium sulphate ($\text{BeSO}_4 \cdot 4 \text{H}_2\text{O}$) were prepared by direct weighing and the strengths checked gravimetrically. 2-Hydroxy-3-naphthoic acid (B.D.H.) was crystallised several times from 60% alcohol until its melting point rose to 222°C. Salicylic and sulpho-salicylic acids were of B.D.H. reagent grade quality. Stock solutions of the acids were standardised by potentiometric titrations with standard caustic potash. Solutions were made up with conductivity water and redistilled absolute alcohol. The potassium salt of 2-hydroxy-3-naphthoic acid was prepared by dissolving the requisite amount of the acid in an equivalent quantity of caustic potash.

pH Measurements were carried out at room temperature ($22 \pm 1^\circ\text{C}$) with a Philips pH-meter (P.R. 9400), standardised against a 0.05 *M* solution of potassium hydrogen phthalate. For the determination of stability constants, the experimental method consisted of potentiometric titrations of acid in the absence and presence of beryllium ions. The dissociation constants of the phenolic protons of the acids in 50% alcohol were determined by potentiometric titrations of acids using standard hydrogen elec-

trode. The first and second dissociation constants of sulphosalicylic acid were determined by Noyes' formula⁸.

A Philips magic eye type (P.R. 9500) conductivity bridge was used for conductivity measurements.

Beryllium 2-hydroxy-3-naphthoic acid complexes

The system was first studied by a precipitation method, and the composition of the precipitates obtained by treating beryllium sulphate solution with increasing molar concentration of $C_{11}H_7O_3K$ determined analytically. At each stage analysis of precipitates after drying at $120^\circ C$ corresponded to $H_2[Be(C_{11}H_6O_3)_2]$, as given in Table III.

TABLE III

No.	Ml of 0.1 M $BeSO_4$	Ml of 0.2 M $C_{11}H_7O_3K$	Added ratio of $C_{11}H_7O_3K$: $BeSO_4$	Amount of precipitate (g)	% Be in precipitate	% $C_{11}H_6O_3$ in precipitate
1	40	10	0.5	0.3531	2.38	97.23
2	40	20	1.0	0.6655	2.34	97.05
3	40	40	2.0	1.4460	2.33	97.58

$H_2Be(C_{11}H_6O_3)_2$ requires: Be = 2.35; $C_{11}H_6O_3$ = 97.12%.

TABLE IV

No.	Ml of 0.1 M $BeSO_4$	Ml of 0.2 M $C_{11}H_7O_3K$	Ml of 0.2 M KOH	Molar ratio of $BeSO_4$: $C_{11}H_7O_3K$: KOH	Amount of precipitate (g)	% Be in compound	% $C_{11}H_6O_3$ in compound
1	40	20	20	1 : 1 : 1	0.6817	3.95	80.80
2	40	40	20	1 : 2 : 1	0.7633	3.98	80.25
3	40	40	40	1 : 2 : 2	clear solution		

$Be(C_{11}H_6O_3)_2 \cdot 2H_2O$ requires: Be = 3.90; $C_{11}H_6O_3$ = 80.52%.

$K_2[Be(C_{11}H_6O_3)_2]$: The resulting solution obtained after the addition of two moles of caustic potash to beryllium sulphate (1 mole) containing two moles of $C_{11}H_7O_3K$, (Table IV, No. 3) was concentrated to about 30 ml. Potassium sulphate was completely separated by adding 100 ml of absolute alcohol to the concentrate. The filtrate was again evaporated on steam bath to saturation point (about 10 ml). A large excess of absolute alcohol was then added. A yellowish white fine needle-like crystalline compound separated out slowly. The compound was washed with alcohol, dried at $110^\circ C$. The analysis corresponded to the formula $K_2[Be(C_{11}H_6O_3)_2]$.

Found: Be = 1.98; $C_{11}H_6O_3$ = 81.45%

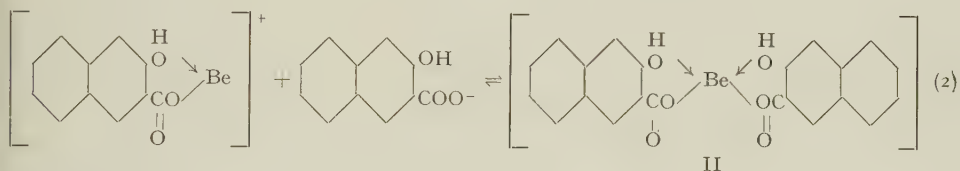
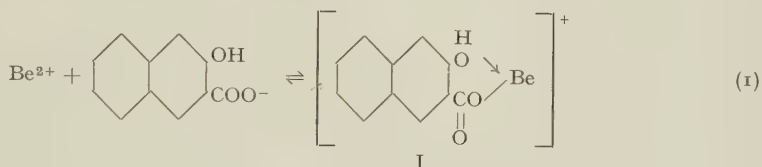
Calcd.: Be = 1.95; $C_{11}H_6O_3$ = 81.23%

In order to observe the effect of a high pH on the 1 : 1 derivative of beryllium with 2-hydroxy-3-naphthoic acid, beryllium sulphate (1 mole) was treated with caustic

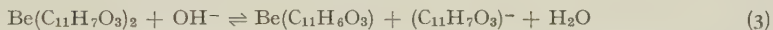
potash (2 moles) in the presence of the potassium salt of the acid (1 mole). It was observed that nearly half the beryllium was precipitated as $\text{Be}(\text{OH})_2$ and the remaining half passed into solution.

DISCUSSION

Precipitation studies of beryllium with potassium 2-hydroxy-3-naphthoate solution in aqueous medium (Table III) have shown that the 1:2 complex is always precipitated irrespective of the amount of $\text{C}_{11}\text{H}_7\text{O}_3\text{K}$ added.



The insoluble nature of the compound (II) favours the equilibrium (2) to such an extent that the equilibrium mixture consists mainly of (II). Neutralisation of the acidic hydrogen of (II) by the addition of one mole of alkali, *i.e.*, raising the pH of the system from about 3.5 to 5.5, leads to the disproportionation of (II) into the 1:1 derivative:

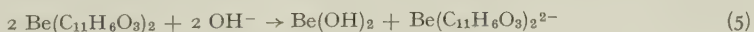


The 2-hydroxy-3-naphthoate ions, $(\text{C}_{11}\text{H}_7\text{O}_3)^-$, liberated in equilibrium (3) combine with any free beryllium ion present in solution to form the 1:1 derivative.:



Thus at a pH of about 5.5, the 1:1 compound was more stable and was always formed even in the presence of excess of $(\text{C}_{11}\text{H}_7\text{O}_3)^-$ ions in solution (Table IV).

At a higher pH (8–9) the 1:2 complex in the ionised form becomes relatively more stable. Thus, in this pH range, the 1:1 derivative formed at a pH of about 5.5 either disproportionates or combines with an excess of 2-hydroxy-3-naphthoate ions, if present, to give the 1:2 complex ion.



or



The above conclusions are supported by the potentiometric and conductometric studies of the systems. Curve 0 (Fig. 1) for the potentiometric titration of beryllium sulphate with alkali is similar to that obtained by BRITTON⁹. Curve 1 (Fig. 1) for the potentiometric titration of the beryllium sulphate with caustic potash in presence of one mole of $\text{C}_{11}\text{H}_7\text{O}_3\text{K}$ shows an inflection at $m = 1$, where m represents moles of base

added per mole of beryllium ion, indicating the formation of 1:1 complex, which then disproportionates into 1:2 complex with the simultaneous precipitation of half the beryllium present in the system as the hydroxide. Thus the second half of the curve 1 (Fig. 1) is a composite of the curve 0 and the second half of curve 2 a sharp inflection occurring at $m = 1.95$. The nature of curve 1' (Fig. 2) for the conductome-

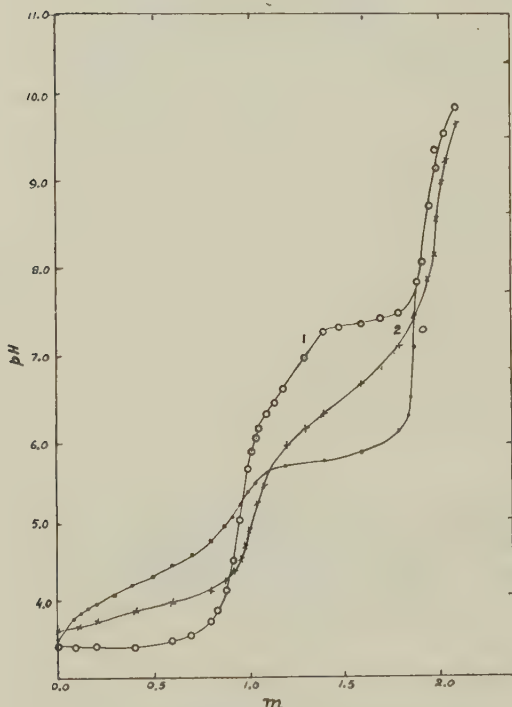


Fig. 1. Potentiometric titration of beryllium sulphate with caustic potash (0.1 *M*) in presence of $C_{11}H_7O_3K$ in aqueous medium: curve 0, $1 \cdot 10^{-2}$ *M* in $BeSO_4$; curve 1, $1 \cdot 10^{-2}$ *M* in $BeSO_4$ and $1 \cdot 10^{-2}$ *M* in $C_{11}H_7O_3K$; curve 2, $1 \cdot 10^{-2}$ *M* in $BeSO_4$ and $2 \cdot 10^{-2}$ *M* in $C_{11}H_7O_3K$. Volume of the reaction mixture before titration was 50 ml. m = moles of base added per mole of beryllium ion.

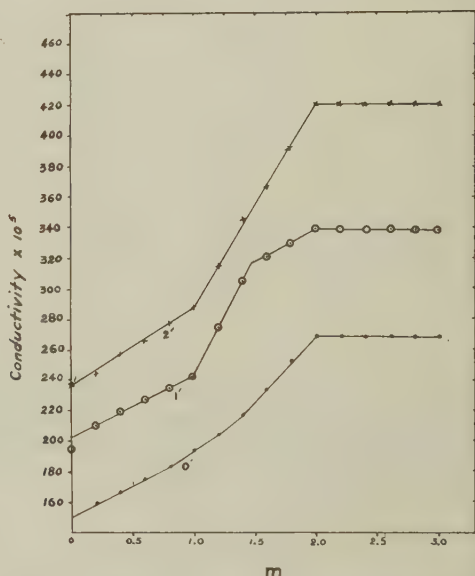


Fig. 2. Curves 0', 1' and 2' represent conductometric titrations of $BeSO_4$ ($1.25 \cdot 10^{-2}$ *M*, 20 ml) with NH_4OH (0.5 *M*) in presence of 0, 1 and 2 moles of $C_{11}H_7O_3K$ (0.25 *M*) respectively. m = moles of base added per mole of beryllium ion.

tric titration of the above system is in complete agreement with the above conclusions. A similar result has been reported by VARMA AND MEHROTRA¹ and also by BANKS AND SINGH⁷ for beryllium salicylate and sulpo-salicylate complexes respectively.

Curve 2 (Fig. 1) for the potentiometric titration of beryllium sulphate with caustic potash in presence of two moles of $C_{11}H_7O_3K$ again shows an inflection at $m = 1$, indicating the formation of 1:1 derivative. At higher pH, the 1:1 complex disproportionates into the soluble 1:2 complex ion and a sharp inflection thus occurs at $m = 2$. Curve 2' (Fig. 2) has also been explained similarly.

In order to investigate the effect of insolubility of beryllium derivatives with 2-hydroxy-3-naphthoic acid in aqueous medium, similar potentiometric titrations were

carried out in 50% alcoholic medium. As the acid was also soluble in the chosen medium, titrations were carried out by starting with the acid, instead of its potassium salt. Figure 3 represents potentiometric titrations of 2-hydroxy-3-naphthoic acid in the presence of 0, 1 and 0.5 moles of beryllium sulphate.

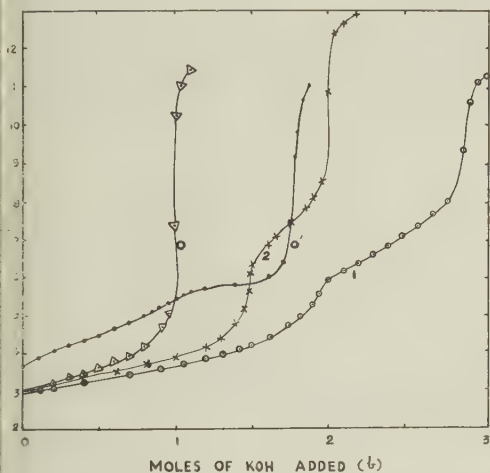


Fig. 3. Potentiometric titration of 2-hydroxy-3-naphthoic acid (50 ml) with KOH (0.1 M) in 50% alcoholic medium: curve 0, $1 \cdot 10^{-2}$ M in $C_{11}H_8O_3$; curve 1, $1 \cdot 10^{-2}$ M in $C_{11}H_8O_3$ and $1 \cdot 10^{-2}$ M in $BeSO_4$; curve 2, $1 \cdot 10^{-2}$ M in $C_{11}H_8O_3$ and $5 \cdot 10^{-3}$ M in $BeSO_4$. Curve 0' represents potentiometric titration of $BeSO_4$ ($1 \cdot 10^{-2}$ M, 50 ml) with 0.1 M KOH in 50% alcoholic medium.

Curve 0 (Fig. 3), shows a sharp inflection at $b = 1$, where b represents equivalents of base added per equivalent of acid, indicating the neutralisation of the carboxylic proton only, the phenolic proton thus remains unaffected under the experimental conditions. Curve 0' is almost similar to that obtained by BRITTON⁹ in the aqueous medium, with the difference that the inflection at one equivalent of base is not very much marked and precipitation appears to be complete at 1.8 instead of 1.9 equivalents of base. The curve 1 shows a sharp inflection at $b = 2$, one mole of base is being consumed by the acid (curve 0) and the other mole is being consumed by the reaction (4). After further addition of alkali, the curve assumes the shape composite of the curve 0' and the latter quarter portion of the curve 2 showing the disproportionation of the 1:1 into the 1:2 complex with the simultaneous precipitation of half the beryllium as hydroxide. Thus in this case the inflection occurs at $b = 2.9$. The curve 2 shows two inflections at $b = 1.5$ (pH 6) and $b = 2.0$ (pH 10), indicating the formation of 1:1 and 1:2 complexes respectively. Hence in 50% alcoholic solutions below pH 6 the more stable 1:1 complex is always formed, which above pH 6 changes into the 1:2 compound.

Stability constants of the compounds were then determined by Bjerrum's method. For comparison, stability constants of beryllium complexes with salicylic and sulphosalicylic acids were also determined under similar conditions.

Calculations of stability constants

If a di-basic acid, H_2A , (2-hydroxy-3-naphthoic and salicylic acids) complexes with beryllium, the reactions may be represented as:



The first and second stability constants k_1 and k_2 will be:

$$k_1 = \frac{[\text{BeA}]}{[\text{Be}^{2+}][\text{A}^{2-}]} \quad (9)$$

$$k_2 = \frac{[(\text{BeA}_2)^{2-}]}{[\text{BeA}][\text{A}^{2-}]} \quad (10)$$

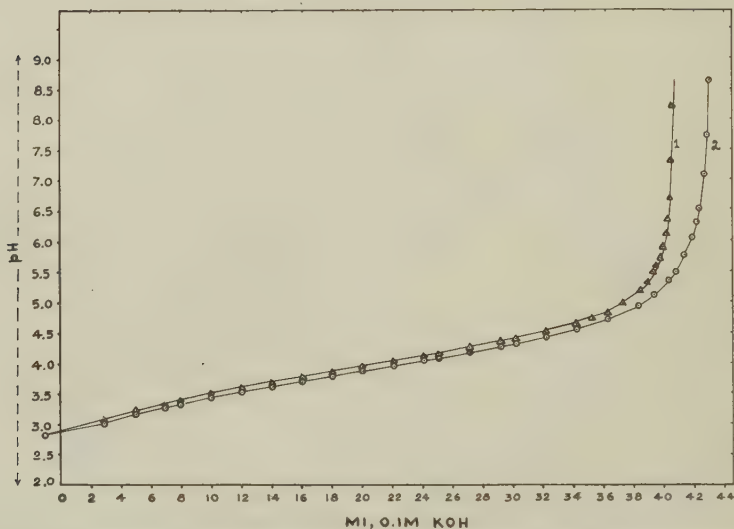


Fig. 4. Curves 1 and 2 represent potentiometric titrations of 2-hydroxy-3-naphthoic acid ($2 \cdot 10^{-2} M$, 200 ml) with 0.1 M KOH in the presence of 5 ml of 50% alcohol and BeSO_4 ($2.5 \cdot 10^{-2} M$) in 50% alcoholic medium.

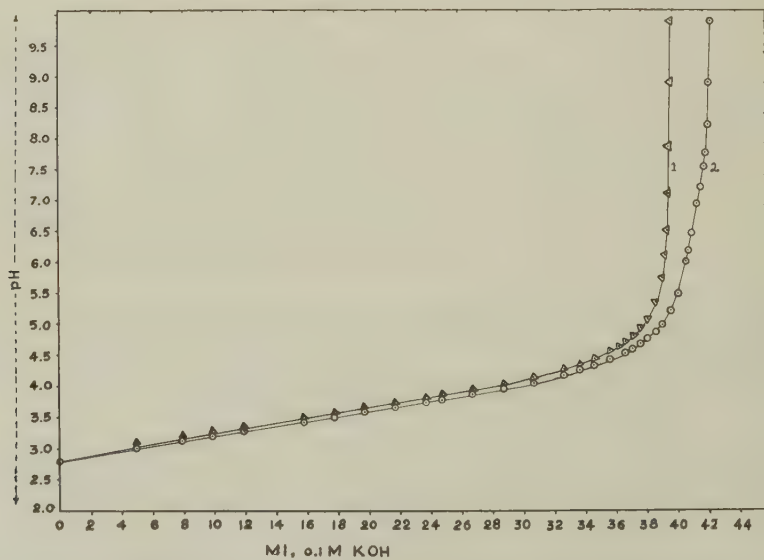


Fig. 5. Potentiometric titrations of salicylic acid ($4.02 \cdot 10^{-2} M$, 100 ml) with caustic potash in the presence of 5 ml of 50% alcohol, curve 1, and BeSO_4 ($2.5 \cdot 10^{-2} M$, 5 ml), curve 2.

and the overall stability constant K will be:

$$K = k_1 k_2 = \frac{[(\text{BeA}_2)^{2-}]}{[\text{Be}^{2+}][\text{A}^{2-}]^2}$$

The values of $\bar{n}$, average number of acid groups (A^{2-}) bound per metal ion, were evaluated from the titration curves of 2-hydroxy-3-naphthoic, salicylic and sulphosalicylic acids (Figs. 4, 5 and 6 respectively), in the absence and presence of beryllium

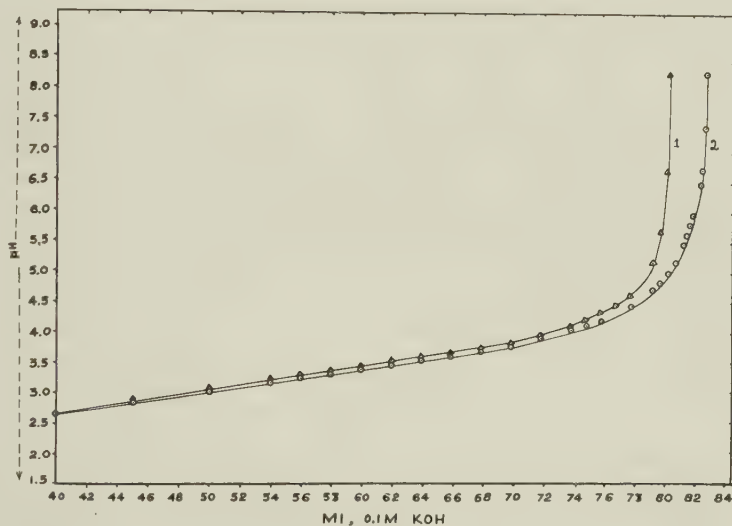


Fig. 6. Curves 1 and 2 represent potentiometric titrations of 5-sulpho-salicylic acid ($4.06 \cdot 10^{-2} M$, 100 ml) with caustic potash (0.1 M) in the presence of 5 ml of 50% alcohol and BeSO_4 ($2.5 \cdot 10^{-2} M$) respectively in 50% alcoholic medium.

ions. The horizontal distance (excess of alkali consumed) between the two curves at any value of pH gave the amount of phenolic proton of the acid liberated by chelation, i.e., the amount of ligand complexed. This value divided by the total amount of the metal ion in the system gave $\bar{n}$. Thus at various values of pH, a set of $\bar{n}$ values was determined.

At any pH, the concentration of ligand (A^{2-}) was calculated as follows:

$$\begin{aligned} [\text{H}_2\text{A}]_{\text{total}} &= [\text{H}_2\text{A}]_{\text{undissd.}} + [\text{HA}^-] + [\text{A}^{2-}] + [\text{BeA}] + 2[(\text{BeA}_2)^{2-}] \\ &= \frac{[\text{H}^+]^2[\text{A}^{2-}]}{K_{a_1}K_{a_2}} + \frac{[\text{H}^+][\text{A}^{2-}]}{K_{a_2}} + [\text{BeA}] + 2[(\text{BeA}_2)^{2-}] \\ [\text{A}^{2-}] &= \frac{[\text{H}_2\text{A}]_{\text{total}} - [\text{BeA}] - 2[(\text{BeA}_2)^{2-}]}{1 + \frac{[\text{H}^+]^2}{K_{a_1}K_{a_2}} + \frac{[\text{H}^+]}{K_{a_2}}} \end{aligned} \quad (11)$$

where K_{a_1} and K_{a_2} represent the first and second dissociation constants of acids, given in Table II. For sulpho-salicylic acid the equation (12) becomes:

$$[A^{3-}] = \frac{[H_3A]_{\text{total}} - [(BeA)^-] - 2[(BeA_2)^{4-}]}{1 + \frac{[H^+]^3}{K_{a_1}K_{a_2}K_{a_3}} + \frac{[H^+]^2}{K_{a_2}K_{a_3}} + \frac{[H^+]}{K_{a_3}}} \quad (12)$$

The values of $\bar{n}$ were then plotted against $-\log[A^{2-}]$ or $-\log[A^{3-}]$ in case of sulpho-salicylic acid, curves 1, 2 and 3 (Fig. 7) for 2-hydroxy-3-naphthoic, salicylic and

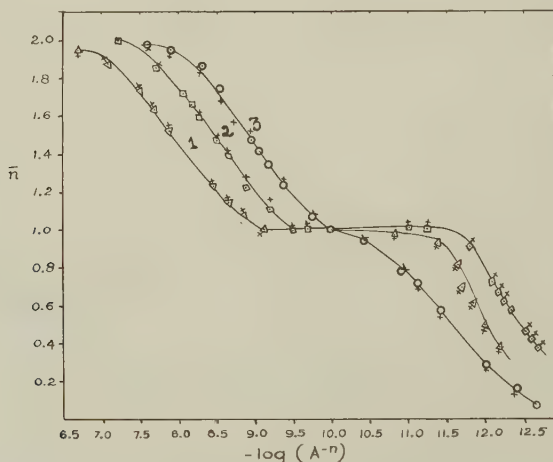


Fig. 7. Degree of formation, $\bar{n}$, as a function of $-\log[\text{ligand}]$: curve 1, beryllium complex of 2-hydroxy-3-naphthoic acid; curve 2, beryllium salicylate; curve 3, beryllium 5-sulphosalicylate complex.

sulpho-salicylic acids complexes respectively. The values of k_1 and k_2 were then adjusted until calculated $\bar{n}$ values, shown by crosses in the figure, were in good agreement with the experimental values. The final constants are given in Table I.

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SELECTIVE DECORATION OF FINE STRUCTURAL EFFECTS IN BERYLLIUM

H. M. LINDSAY, V. D. SCOTT AND A. MOORE*

Atomic Weapons Research Establishment, Aldermaston, Berkshire (Great Britain)

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SUMMARY

A new chemical method to reveal sub-microscopic structural effects in beryllium, such as iron-rich precipitates developed during ageing, has been developed. The method involves an ion-exchange reaction in which copper decorates localized regions in the metal and it is simply carried out by immersing the metallographic surface in an orthophosphoric acid solution containing dissolved copper. The metallographic features have been correlated using optical microscopy, electron microscopy and electron probe microanalysis. Some indication of the wider application to other metal systems is given.

INTRODUCTION

Recently, a precipitation ageing process has been reported^{1,2} to occur in commercial grade beryllium and it was concluded that the behaviour of the metal after heat treatment was dependent upon the nature and quantity of impurity present. In view of these observations it became necessary to develop a metallographic procedure whereby fine-scale structural effects such as sub-microscopic precipitates could be detected and studied. During the course of the work a new chemical technique was discovered which, in contrast to the more conventional etching procedures, involved depositing material from a solution containing copper ions, on to highly localized regions of the metallographically-prepared specimen surface. In this way sub-microscopic structures were decorated with a relatively coarse deposit which could be resolved in the optical microscope. These results suggested that a principal condition for decoration to take place is that the decorant should be more electronegative than the region which it is decorating.

Examples are given for beryllium containing 0.18 wt.% iron and which show the sensitivity of a particular decorant (copper) in revealing optically fine-scale structural effects that are normally only detected using electron microscopy. The more general application of this technique, using the same solution, is illustrated by similar decoration effects on centres in aluminium containing ~0.4 wt.% iron.

EXPERIMENTAL DETAILS

Beryllium

Figures 1 and 2 are electron micrographs of Au-Pd shadowed replicas which were taken from beryllium containing 0.18 wt.% iron in the aged and over-aged conditions respectively. The surfaces were prepared by mechanical polishing and then etching in

a solution of 5% HF in glycerol. The zone of particles, 0.1 to 0.3 μ diameter, surrounding the grain boundaries (Fig. 1), which were not resolvable directly using optical microscopy, were found, from the direction of replica shadowing, to stand in relief from the surface. Figure 2 shows a typical over-aged microstructure with large grain-boundary precipitates. Examination of these metallographic surfaces in the electron probe X-ray micro-analyser showed that on over-ageing there is a migration of iron to the grain boundary and it may be concluded that the interstage precipitates surrounding grain-boundaries in the aged beryllium are also iron-rich. The precipitate in

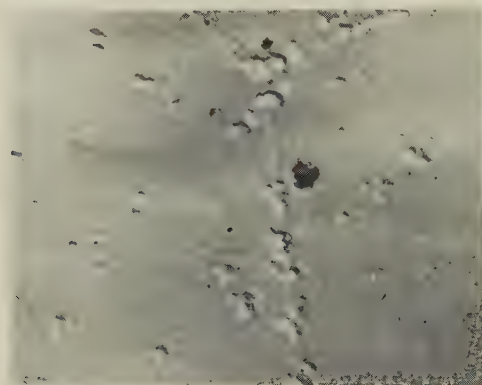


Fig. 1. Aged Be-0.18 wt.% Fe, showing concentration of precipitate near grain boundaries. Shadowed replica. ($\times 8,000$)



Fig. 2. Over-aged Be-0.18 wt.% Fe, showing coalescence of precipitate on grain boundaries. Shadowed replica. ($\times 8,000$)



Fig. 3. Aged Be-0.18 wt.% Fe. X-ray image taken in Fe $K\alpha$ radiation ($\times 800$)



Fig. 4. Over-aged Be-0.18 wt.% Fe, showing coalescence of precipitate on grain boundaries. X-ray image taken in Fe $K\alpha$ radiation. ($\times 800$)

the aged condition, however, is too small to be resolved by the micro-analyser. Figures 3 and 4 are scanning X-ray images taken in Fe $K\alpha$ radiation from the two specimens of beryllium illustrated in Figs. 1 and 2 respectively.

Immersion of these metallographic beryllium surfaces for 15 sec in orthophosphoric acid containing copper ions caused decoration of fine-scale structural effects which

rendered them visible in the optical microscope. A suitable concentration of copper ions in the orthophosphoric acid has been obtained by electropolishing copper in the solution for 1 h at 1.5 V and 0.1 amps/cm². Optical micrographs corresponding to Figs. 1 and 2 respectively are reproduced in Figs. 5 and 6. The decorant could be removed by wiping with a dry selvyt cloth and its distribution reproduced exactly by re-immersion in the copper-orthophosphoric acid solution.

Identification of the metallic elements present in the deposited particles has been

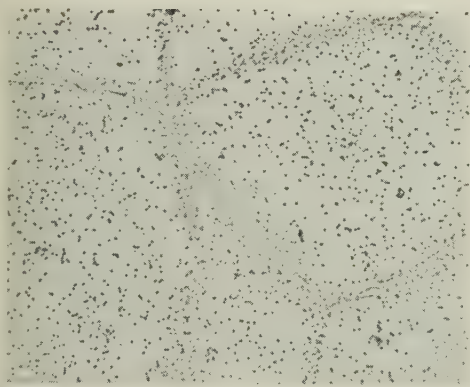


Fig. 5. Aged Be-0.18 wt.% Fe, showing concentration of precipitate near grain boundaries. Surface decorated with copper. Optical micrograph. ($\times 800$)

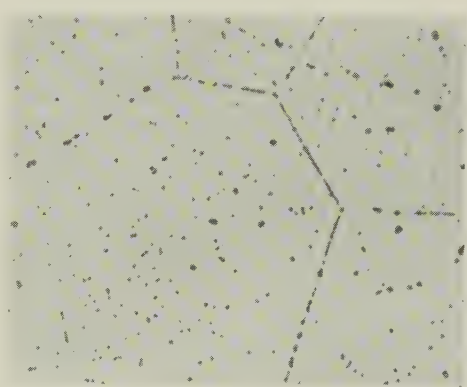


Fig. 6. Over-aged Be-0.18 wt.% Fe, showing coalescence of precipitate on grain boundaries. Surface decorated with copper. Optical micrograph. ($\times 800$)

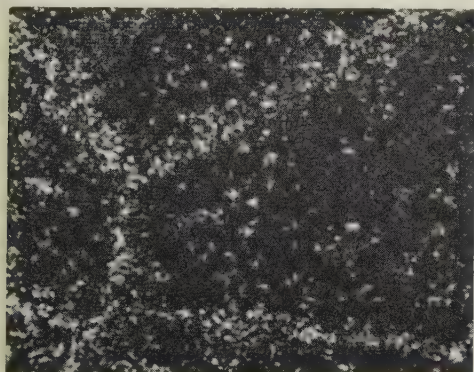


Fig. 7. Aged Be-0.18 wt.% Fe, showing concentration of precipitate near grain boundaries. Surface decorated with copper. X-ray image taken in Cu $K\alpha$ radiation. ($\times 800$)

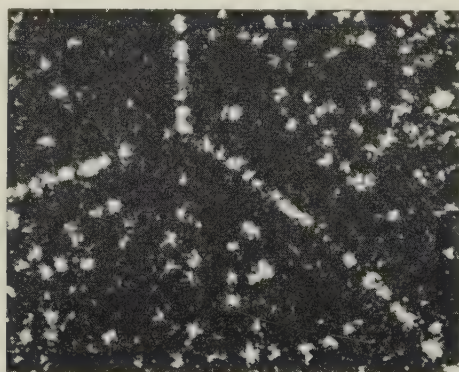


Fig. 8. Over-aged Be-0.18 wt.% Fe, showing coalescence of precipitate on grain boundaries. Surface decorated with copper. X-ray image taken in Cu $K\alpha$ radiation. ($\times 800$)

clearly demonstrated using microprobe analysis. Figures 7 and 8 are scanning X-ray images taken in Cu $K\alpha$ radiation which correspond to the optical micrographs, Figs. 5 and 6 respectively and are, in fact, the same fields as shown in Figs. 3 and 4. Heavy decoration with copper on grain boundaries rich in iron is clearly seen in the over-aged beryllium, Fig. 8.

In general, no elements other than copper were identified at the deposition sites; the range studied included elements of atomic number ≥ 21 . The dendritic nature of the deposit growth is illustrated in the extraction replica electron micrograph shown in Fig. 9. Examination of such growths produced on single crystals of known orientation showed no apparent preferred crystallographic growth direction. Diffraction patterns indicated they possessed an amorphous structure. The mean diameter of deposits ranged from $0.5\text{--}1.5\ \mu$.

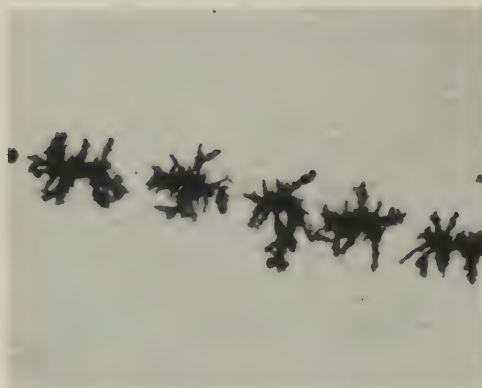


Fig. 9. Extracted particles from decorated surfaces. Electron micrograph. ($\times 8,000$)

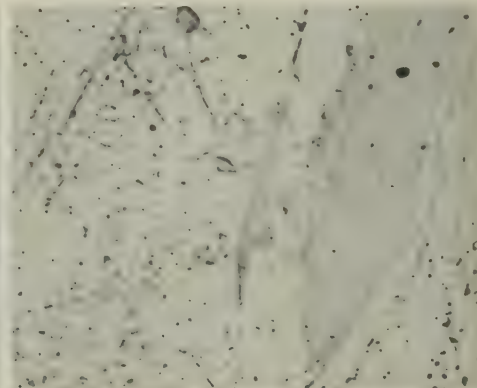


Fig. 10. Warm-worked beryllium structure decorated with copper. Optical micrograph. ($\times 800$)

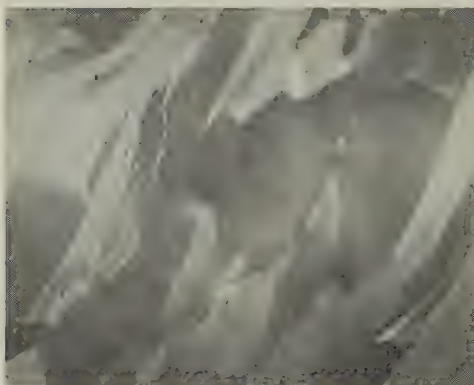


Fig. 11. Warm-worked beryllium structure viewed in polarised light. Optical micrograph. ($\times 400$)

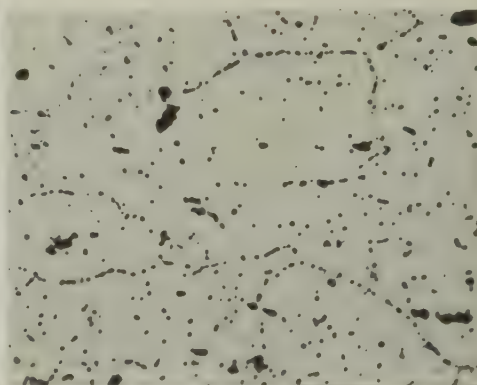


Fig. 12. Commercially pure aluminum containing 0.4 wt.% iron. Surface decorated with copper. Optical micrograph. ($\times 800$)

Figure 10 shows the effect that stress in the metal can have on the behaviour of the decorant. The metal grains, when viewed in polarized light Fig. 11 exhibited a typical warm-worked beryllium structure. Areas of local work were decorated intensely, but very finely, which contrasts with the generally more coarse dissemination which

characterises an annealed or hot-worked structure. It would appear necessary, therefore, to take account of local stress conditions when interpreting the significance of a particular decoration effect.

General

To investigate further the location of impurity at the deposit sites, a series of experiments were carried out to study whether an electrochemical displacement reaction took place. Immersion of a series of metallographically-prepared surfaces of pure metals into the copper-orthophosphoric solution indicated that an electrochemical effect was probably associated with the decorating reaction. Deposition of copper occurred on metals above copper in the electrochemical series (for example, zinc, iron, tin, cadmium, lead and manganese) but not on more electropositive elements (silver and gold). The only exception to this empirical rule was super-pure aluminium on which no deposition occurred. By contrast, however, a commercial grade of aluminium containing 0.4 wt. % iron was decorated in a manner analogous to beryllium containing 0.18 wt. % iron (see Fig. 12).

CONCLUSIONS

It has been clearly demonstrated how fine-scale structural effects in beryllium which are too small to be resolved directly in the optical microscope can be revealed by decorating them with copper as precipitated from a solution of orthophosphoric acid.

Illustrations included in this account show (a) preferred nucleation of precipitates in grain-boundary regions, (b) subsequent coalescence of the precipitates on over-ageing particularly at grain boundaries and (c) denudation of a zone $> 10 \mu$ wide adjacent to grain boundaries on over-ageing.

It is believed that an ion exchange reaction is associated with the decoration and as such copper deposition has been observed on other metals more electropositive than the decorant. It is concluded that the presence of highly-localized regions of iron is mainly responsible for the decoration effects, but it is to be expected that local stress concentrations may well affect the response of any decorant. Nevertheless, the present work gives a clue to a new and more selective procedure in metallographic practice.

ACKNOWLEDGEMENTS

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RECOVERY IN COLD-WORKED TUNGSTEN

R. C. KOO

Research Dept., Lamp Division, Westinghouse Electric Corporation, Bloomfield, N.J. (U.S.A.)

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SUMMARY

Recovery in cold-worked powder metallurgy tungsten of two different purity levels was investigated by means of dislocation etch-pitting, accompanied by tensile measurements at 600°C, hardness measurements at room temperature, and X-ray back reflection. It was found that polygonization and subgrain coarsening in high-purity tungsten occurred readily at relatively low annealing temperatures. Above 1100°C strain-induced grain boundary migration occurred extensively in addition to subgrain coarsening. The presence of 25-63 weight p.p.m. of aluminum had a large effect in retarding polygonization and subgrain growth and raised the recrystallization temperature from 1400°C to 1800°C. However, strain-induced grain boundary migration was insensitive to the presence of aluminum at this concentration.

Tensile measurements at 600°C showed that the subgrain size played a dominant role in the recovery of yield stress. Furthermore, the variation of the lower yield stress with subgrain diameter in annealed but unrecrystallized specimens obeyed the Petch equation $\sigma_{LY} = \sigma_0 + k_Y d^{-1/2}$, giving a value of $3.3 \cdot 10^7$ dynes/cm^{3/2} for k_Y . This suggests that the subgrain boundaries behave much in the same way as the grain boundaries in acting as barriers for dislocations.

INTRODUCTION

Recent experiments on recovery in cold-worked tungsten have distinguished recovery which results from the disappearance of lattice point defects from recovery which results from the annihilation and rearrangement of dislocations. KOO¹ and SCHULTZ² independently attribute the recovery of electrical resistivity at annealing temperatures below 400°C to the annealing-out of single vacancies with an activation energy of 1.7 eV, and above 400°C to the annihilation and rearrangement of dislocations. That rearrangement of dislocations begins at temperatures as low as 400°C has been confirmed recently by WEISSMAN³. He found direct evidence of dislocation rearrangement by means of X-ray and electron transmission microscopy.

In a similar experiment on the recovery of electrical resistivity in cold-worked tungsten wire, NEIMARK AND SWALIN⁴ showed further that the addition of small amounts of aluminum and silicon raised the activation energy for the annealing-out of single vacancies from 1.7 eV to 2.3 eV. They interpreted this as evidence of trapping of vacancies by impurity atoms.

Experimental observations on the effects of impurities on the changes in microstructure and mechanical properties upon annealing heavily drawn wires above 600°C have been rather extensive in the literature^{5,6,7,8}. Unfortunately, all the detailed studies reported were carried out on heavily worked wires^{5,7,8} or foils⁶

where it is exceedingly difficult, if not impossible, to ascertain whether the observed changes in microstructure due to annealing were a result of polygonization, subgrain coarsening, strain-induced grain boundary migration or even recrystallization. Therefore, the effects of impurities on these mechanisms have not been clearly distinguished. The present study was undertaken (a) to evaluate by a dislocation etch-pit technique the effects of small amounts of metallic impurities as well as the effect of the amount of prior deformation on the various mechanisms of recovery above 600°C and (b) to elucidate the effect of substructure on the recovery of mechanical properties.

MATERIALS AND TEST METHODS

Three lots of high-purity powder metallurgy tungsten designated A, B, and C were prepared by sintering, swaging, and then grinding into rods 0.30 in. in diameter. The final swaging temperature prior to grinding was in the range 1300°C–1500°C. For the studies of the effect of the amount of prior deformation on recovery, material A was fabricated into two groups having a 50% and 80% reduction in area. The B lot had 80% and the C lot had 50% reduction in area. Analyses on the sintered ingots and the finished rods showed that the C contained substantially higher quantities of aluminum than the B (see Table I).

TABLE I
IMPURITY ANALYSES (wt. p.p.m.) ON TUNGSTEN SINTERED INGOTS AND RODS

Sample	Form	Mn	Al	Fe	Si	Mg	Ni	Ca	K	C	H	O	N
Material A	Sintered ingot	<2	5	38	30	<3		10	10	70	2	9	8
Material B	Sintered ingot	<2	5	38	14	<3	<3	5	7.5	30	6	7	9
Material C	Sintered ingot	<2	63	61	31	6	22	<2	<1	20	3	12	5
Material A (50%)	Rod	<2			39						3	7	3
Material A (80%)	Rod	<2	5	14	7	<3	16	20	15	40	3	4	15
Material B	Rod	<2	6	51	14	<3	<3	<5	<1	10	4	4	7
Material C	Rod	<2	25	64	5	6	<3	<2	<1	10	2	11	5

The rods were shaped into tensile test specimens having a 1.50 in. gauge length and 0.18 in. gauge diameter by centerless grinding. Two tensile specimens of each lot were annealed in a vacuum of $1 \cdot 10^{-4}$ mm of Hg for 30 min at each temperature from 800°C up, at 100°C–150°C intervals. The annealed specimens were pulled at a strain rate of $8 \cdot 10^{-5}$ /sec with automatic recording of load–elongation curves. In order to ensure that ductile behavior would be exhibited by all specimens, a test temperature, 600°C, well above the tensile transition temperature range of 200°C to 400°C, was chosen⁹. All tests were made in an argon atmosphere to prevent surface oxidation. The undeformed shoulders of the broken tensile specimens were sectioned longitudinally, electropolished and etched in a 5% KOH solution to reveal dislocation etch-pits. Evidence that the etch-pits developed locate the sites of emergence of dislocations is given in the APPENDIX. After metallographic examination, hardness measurements and X-ray back reflection photographs were taken on the same samples.

EXPERIMENTAL RESULTS

Recrystallization in these materials was characterized by the development of equiaxed grains free of substructure detectable by etch-pitting, accompanied by a large decrease in hardness and yield stress. The recrystallization temperatures found for the four lots of material by means of metallographic examinations are listed in Table II.

TABLE II
RECRYSTALLIZATION TEMPERATURES

<i>Material</i>	<i>Reduction in area</i>	<i>Recrystallization temperature</i>
A	80%	1400°C-1450°C
A	50%	1425°C-1475°C
B	80%	1375°C-1425°C
C	50%	1775°C-1825°C

The recrystallization temperature was substantially the same for all lots of material except C. Furthermore, the recovery characteristics, as studied by the various parameters of material A having 80% and 50% reduction in area, were identical. It was concluded that there was no effect of cold work on either recovery or recrystallization for the two different amounts of deformation studied. This is understandable since neither was recrystallized during swaging, so that the total strain was large as compared with the percentage of difference in strain. Therefore, the results of A and C materials will be discussed in detail to demonstrate the impurity effects observed.



Fig. 1. Material A, unannealed. ($\times 2000$)

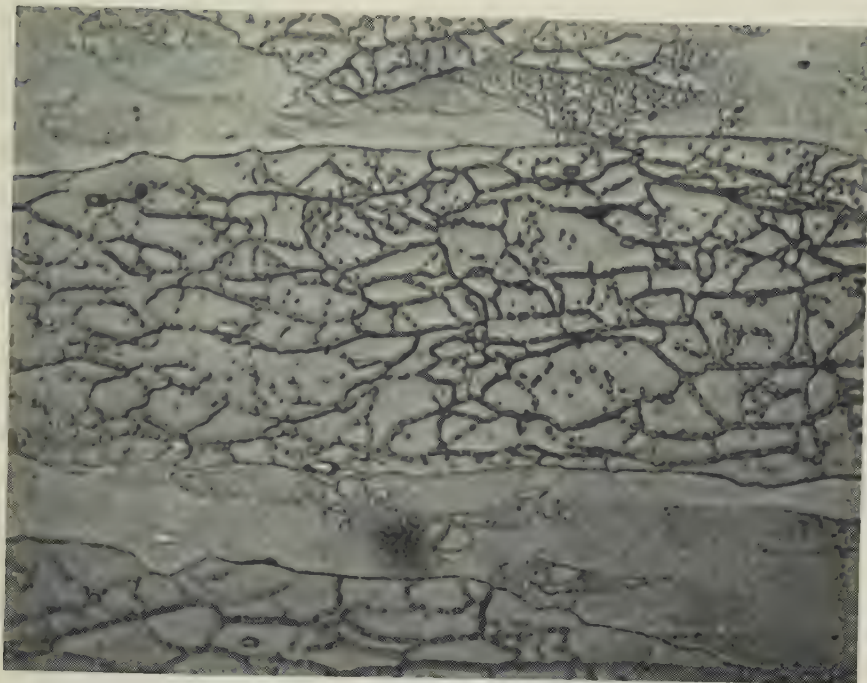


Fig. 2a. Material A, annealed at 800°C. ($\times 2000$)

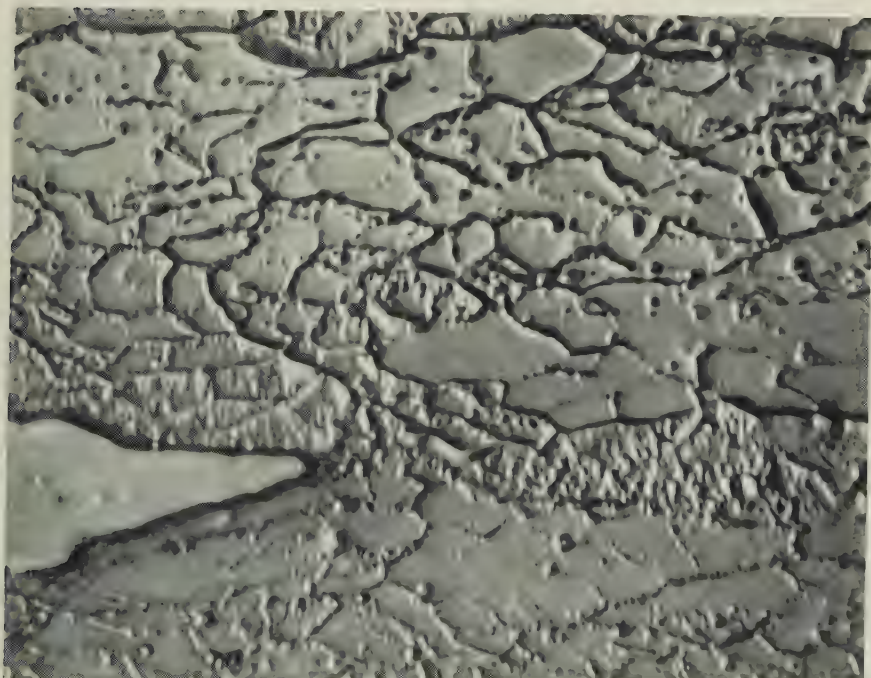


Fig. 2b. Material A, annealed at 1200°C. ($\times 2000$)



Fig. 3a. Material C, annealed at 800°C. ($\times 2000$)

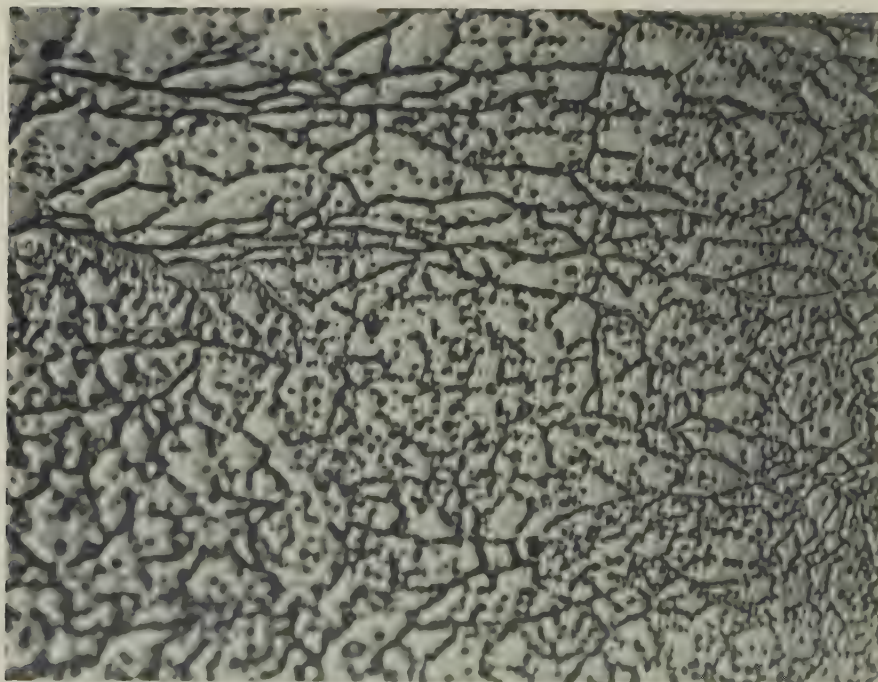


Fig. 3b. Material C, annealed at 1300°C. ($\times 2000$)

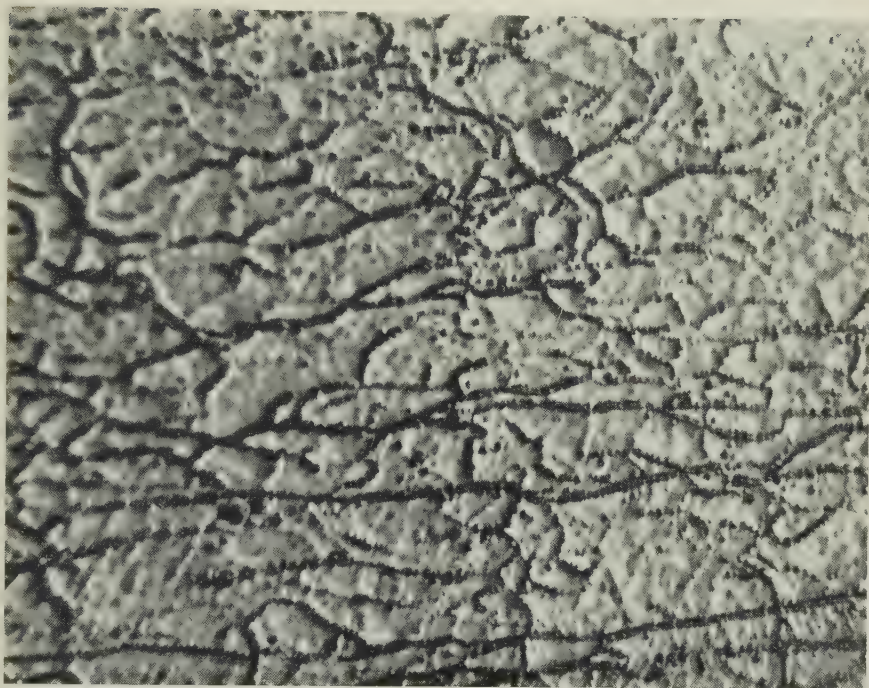


Fig. 3c. Material C, annealed at 1500°C. ($\times 2000$)

Metallography

Changes in substructure have been observed distinctly in the course of annealing with etch-pits. The dislocations in the unannealed specimens appear to be mostly at random although some degree of short-range alignment of dislocations is evident, as shown in Fig. 1. The average density of dislocation etch-pits in the unannealed sample was low, only about $5 \cdot 10^8/\text{cm}^2$.

The partial alignment of dislocations and the low density of dislocations in the unannealed specimens are presumably a result of the relatively high temperature (1300°C–1500°C) at which the material was worked.

Annealing the higher purity A material at 800°C produced marked changes in dislocation structure. A highly polygonized substructure was formed in at least 90% of the area (Fig. 2a) and the density of etch-pits decreased to $\sim 2 \cdot 10^8/\text{cm}^2$. Upon increasing the annealing temperature up to recrystallization, subgrain coarsening occurred progressively (Fig. 2b) with a small increase in disorientation of the subgrains. It was estimated from the etch-pit counts that in the course of annealing from 800°C to 1300°C, the increase in disorientation of most of the subgrain boundaries was from 1–3 min of arc to 4–7 min of arc and the average density of dislocation etch-pits decreased to $\sim 1 \cdot 10^8/\text{cm}^2$.

Similar metallographic studies of the C material showed that the impurities retard this annealing process. Typical changes in substructure of the C specimens annealed at various temperatures are shown in Figs. 3a, 3b and 3c.

Comparisons of these photomicrographs with those of the higher purity material A

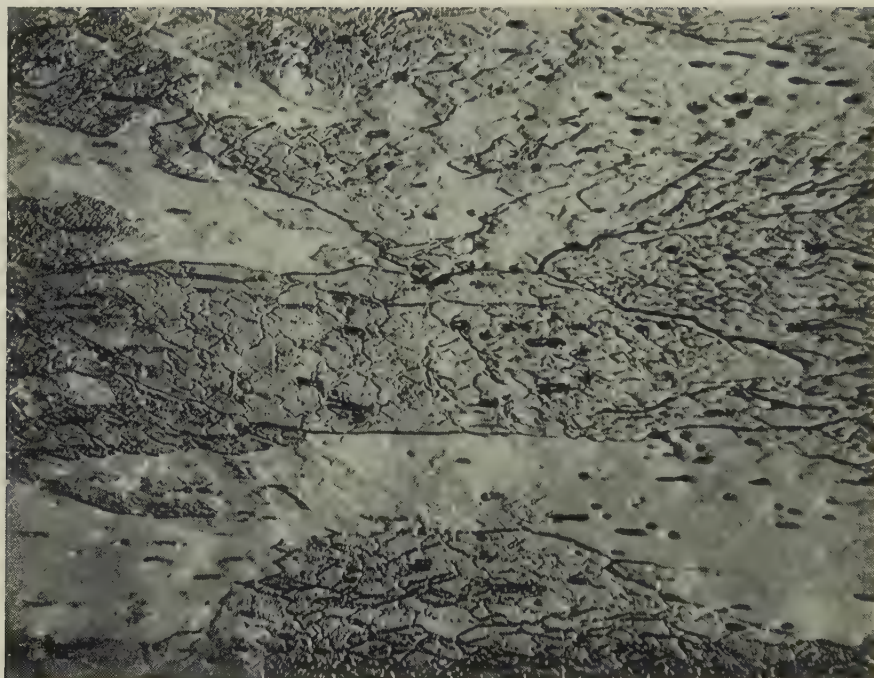


Fig. 4a. Material A, annealed at 1000°C. ($\times 500$)

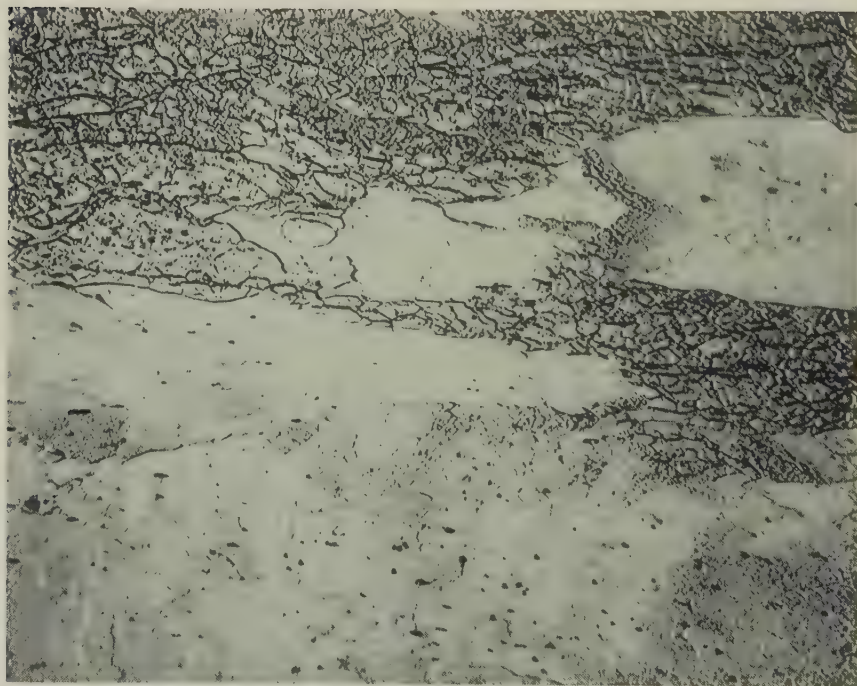


Fig. 4b. Material A, annealed at 1350°C. ($\times 500$)



Fig. 5a. Material C, annealed at 1000°C. ($\times 500$)

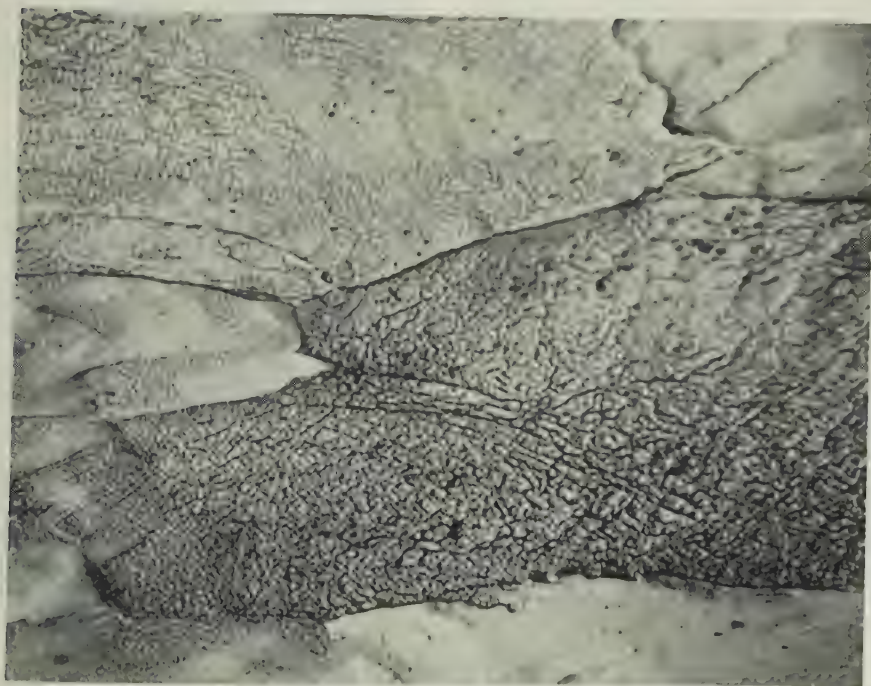


Fig. 5b. Material C, annealed at 1300°C. ($\times 500$)

reveal the effect of impurities on the annealing process. For example, Fig. 3b shows that, even in specimens annealed at 1300°C , the substructure was not fully polygonized and still had an etch-pit density of $\sim 3 \cdot 10^8/\text{cm}^2$. In general, the lower purity C differs from the high purity A material in that both polygonization and subgrain coarsening were markedly retarded and that a high density of random dislocations was retained.

Considerable strain-induced grain boundary migration occurred above 1100°C in all the materials studied, in addition to subgrain growth. This is shown in Fig. 4 for material A and in Fig. 5 for material C. The strain-induced grain boundary migration was particularly noticeable in the direction normal to the rod axis, resulting in a reduction in the number of grains. Differences in the density of dislocation etch-pits of $2 \cdot 10^8/\text{cm}^2$ between neighboring grains were observed in all specimens annealed

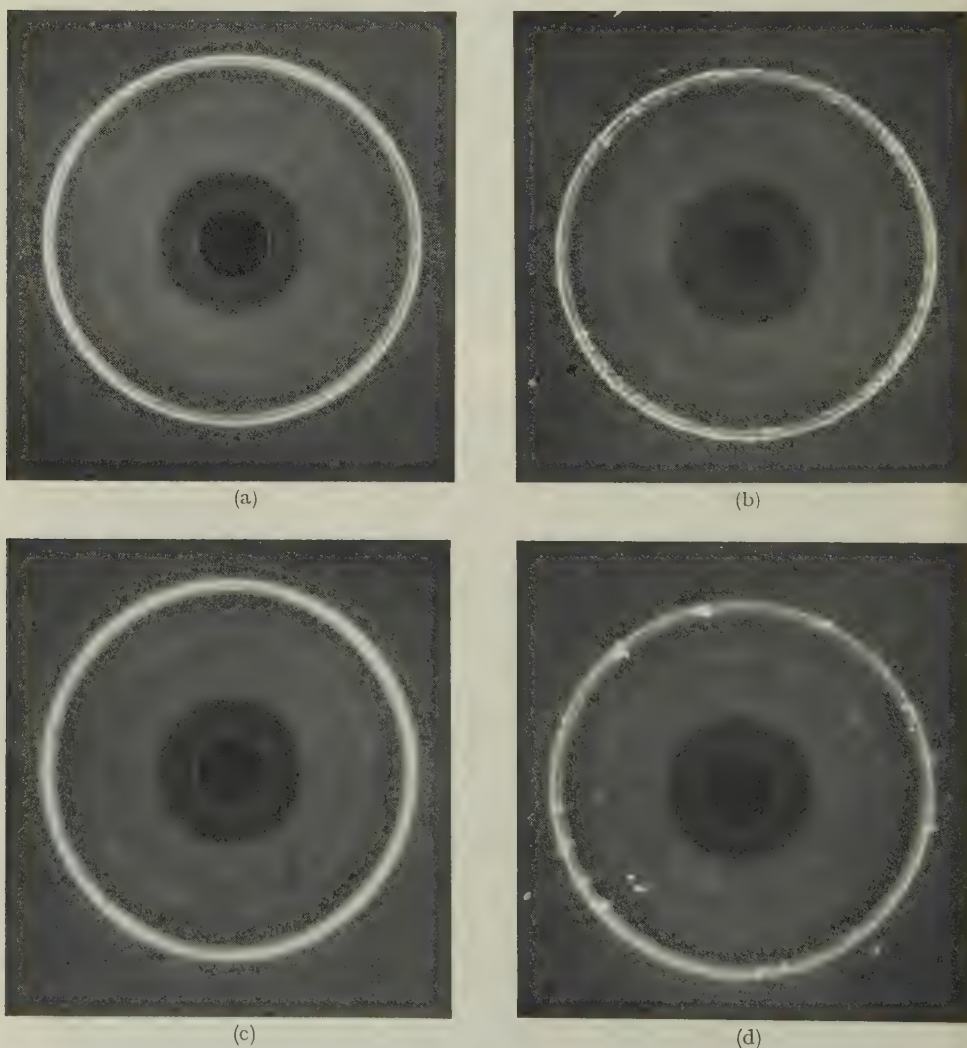


Fig. 6. X-ray back reflection photographs. (a) Material A, annealed at 1100°C ; (b) Material A, annealed at 1350°C ; (c) Material C, annealed at 1100°C ; (d) Material C, annealed at 1300°C .

at temperatures of 1100°C and higher. Furthermore, similar variations from one area to another within single grains were also found, especially in material C. It is significant to note that, in spite of the retardation in the formation and growth of subgrains in material C, appreciable amounts of strain-induced grain boundary migration still occurred, as shown in Fig. 5. Therefore, strain-induced grain boundary migration appeared to be relatively insensitive to the impurities in this material. This will be discussed more in detail in a later section.

X-ray back reflection photographs provided additional evidence for extensive strain-induced grain boundary migration in both materials. As the annealing temperature increased above 1100°C spots appeared on the Debye-Scherrer rings and became very intense for specimens annealed at 1300°C , as shown in Fig. 6.

These results confirm the metallographic observations discussed in the preceding paragraph.

The generalizations which can be drawn from the metallographic studies described in the preceding paragraphs are the following:

1. The density of dislocation etch-pits in the as-swaged rod is rather low, approximately $5 \cdot 10^8/\text{cm}^2$.
2. The main process of annealing is polygonization and subgrain growth.
3. Strain-induced grain boundary migration occurs extensively at annealing temperatures above 1100°C .
4. Small amounts of impurities have a large effect in retarding polygonization and subgrain growth and in raising the recrystallization temperature. Strain-induced grain boundary migration is, however, insensitive to these impurities.

Mechanical properties

Measurements of yield stress at 600°C and hardness at room temperature were made on all specimens annealed up to 1500°C . Intergranular cracks parallel to the tensile axis were found in most of the annealed but unrecrystallized specimens of material C, with some of them running from the middle of the specimen into one shoulder. It is believed that this is due to the presence of grain boundary precipitates which lowered the effective surface energy for crack propagation. All specimens annealed at temperatures up to 1300°C exhibited a well-defined yield point, but specimens annealed at temperatures above 1300°C did not show a yield point. The yield stress data for both materials are plotted in Fig. 7. In this figure, the upper yield stress is used for specimens with a yield point; the stress at 0.2% offset is used for specimens without a yield point. The hardness data are not listed since the recovery of hardness followed the same pattern as that of the yield stress. That the recovery of yield stress for material A having 80% and 50% reduction in area is the same again indicates that the difference in the amount of cold work had a negligible effect. The yield stress for material C, however, recovered only slightly after annealing at temperatures up to 1500°C , but material A showed substantial recovery at annealing temperatures far lower (Fig. 7). This is in agreement with the differences in substructure in the two materials revealed by the metallographic studies discussed earlier. Again it is proposed that this difference in the recovery of the yield stress is caused by differences in impurities in the two materials.

A good quantitative correlation was found to exist between yield stress and subgrain size rather than grain size in the annealed but unrecrystallized specimens. The

lower yield stress for the annealed but unrecrystallized specimens of materials A and B is plotted in Fig. 8 against the inverse square root of subgrain diameter. The average

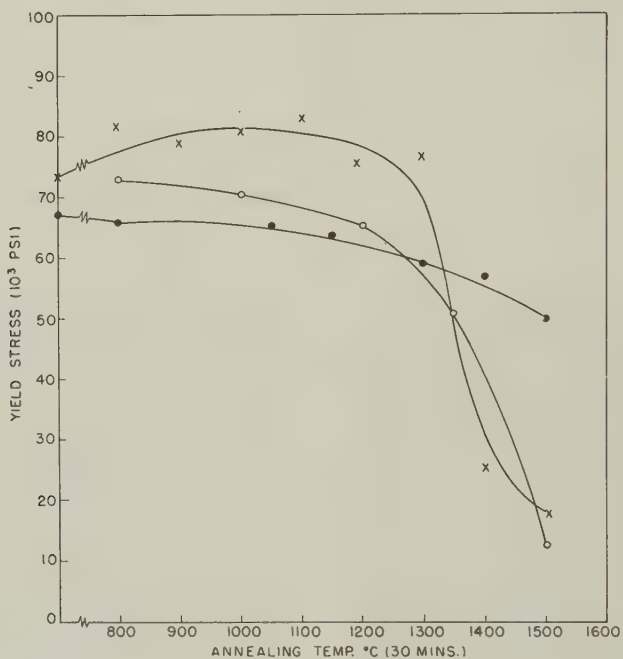


Fig. 7. Yield stress in tension at 600°C vs. annealing temperature. $\times$, Material A (80%); $\circ$, material A (50%); $\bullet$, material C.

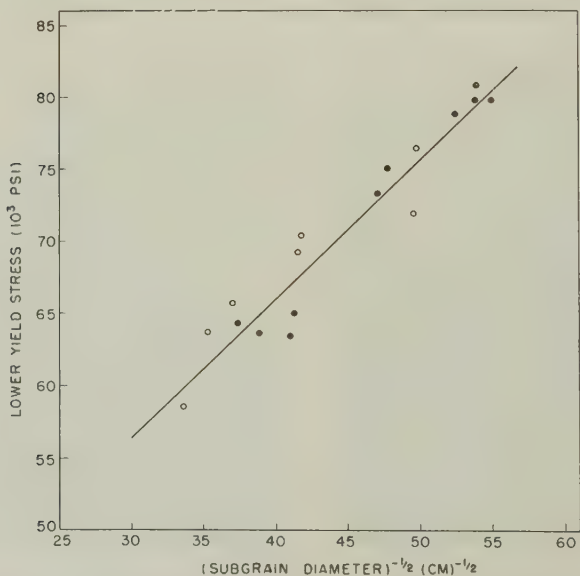


Fig. 8. Variation of lower yield stress with subgrain diameter for specimen extended at 600°C. $\bullet$, Material A (80% red.); $\circ$, material B (80% red.).

subgrain diameter was determined by the linear intercept method. Data on material C are not included in the plot because of uncertainties in determining the subgrain size, since it was not fully polygonized in most specimens. Fig. 8 shows that the variation of the lower yield stress, σ_{LY} , with subgrain diameter, d , obeys the Petch equation¹⁰

$$\sigma_{LY} = \sigma_0 \times k_Y d^{-1/2}$$

where σ_0 is the stress resisting the movement of unlocked dislocations, and k_Y is a measure of the stress to unlock dislocations from their Cottrell atmosphere^{11,12}. The straight line in Fig. 8 is drawn by using the method of least squares, the correlation coefficient being 0.97. Values found for k_Y and σ_0 in shear (one-half of the values in tension) are $3.3 \cdot 10^7$ dynes/cm^{3/2} and 13,000 p.s.i. respectively.

DISCUSSION

The significant results of the present experiments are:

1. Although a small amount of impurities has a large effect in retarding the rate of polygonization and subgrain growth, extensive strain-induced grain boundary migration occurred in both pure and impure materials.
2. The variation of the lower yield stress with subgrain size at 600°C obeys the Petch equation.

It remains now to examine (a) those factors which may account for the detailed differences in the various mechanisms of recovery as affected by impurities and (b) the implications which may be derived from the observed relationship of lower yield stress and subgrain size.

Polygonization and strain-induced grain boundary migration

Results of the metallographic studies have shown that annealing of cold-worked tungsten of high-purity at 800°C results in a highly polygonized substructure. It is not surprising that polygonization could occur in tungsten at such a low homologous temperature, since in the b.c.c. metals at least the dislocations lying along the $\{110\}$ planes are not expected to be extended¹³. This greatly facilitates the climb of edge dislocations¹⁴ and the glide of screw dislocations out of their original glide planes¹⁵. Evidence that the screw dislocations in a b.c.c. metal can glide freely without being confined to one slip plane has been provided by LOW AND GUARD in silicon ferrite¹⁶.

The differences in recovery between materials A and C can be traced to the differences in impurities in these materials. It appears that the higher levels of Fe, Al, and O₂ (see Table I) in material C could be responsible for the retardation in polygonization and subgrain growth. Nevertheless, the effects observed cannot be attributed to Fe, or O₂. A similar amount of Fe was found in material B, yet its recovery and recrystallization behavior were identical to material A. Furthermore, unpublished work on the effect of oxygen on recrystallization in tungsten in this laboratory and also in the Osram Laboratory in Germany has firmly established that oxygen at the levels found in the materials used does not raise the recrystallization temperature. Thus, the observed effects appear to be caused by aluminum. This is in agreement with the experimental findings of NEIMARK AND SWALIN⁵, mentioned earlier.

There is some indication that grain-boundary precipitates were present in material C. Intergranular cracks parallel to the tensile axis were found in almost all tensiles

of material C with some of them running from the middle of the specimen into one of the shoulders. It is believed that this was due to the grain boundary precipitates which lowered the effective surface energy for crack propagation.

That the observed strain-induced grain boundary migration was not affected by impurities is markedly different from the well-known inhibiting effect of precipitates on grain growth in a recrystallized material¹⁷. This difference in the grain boundary mobility is presumably due to the large difference in the driving force available for the two types of migration. For strain-induced grain boundary migration, there exists a large difference in strain energy across the grain boundary serving as the major driving force, but in normal grain growth such strain energy differences are virtually absent. Thus, in the present case of strain-induced grain boundary migration, the total driving force available due to the difference in strain energy density across the grain boundary and the grain boundary force (which depends on whether the boundary migrates toward or away from its center of curvature as well as the grain boundary energy¹⁸) must be large enough to overcome the restraining force exerted by the precipitates. Similarly, it may be expected that recrystallization would be equally insensitive to small amounts of second-phase impurities. This view has been proposed recently by LUCKE AND DETERT¹⁹.

A rough estimate of the difference in strain-energy density across a grain boundary can be made. A typical observed difference in etch-pit density between two neighboring grains in a specimen of material C annealed at 1300°C is $2 \cdot 10^8/\text{cm}^2$. If randomly orientated dislocations are assumed, a volume correction factor of 2 may be used to obtain the total length of $4 \cdot 10^8 \text{ cm}/\text{cm}^3$. The strain energy of a single edge dislocation in a cylinder of radius r_1 , as given by COTTRELL²¹ is:

$$\frac{\mu b^2}{4\pi(1-\nu)} \left[\log \left(\frac{r_1}{r_0} \right) - 1 \right]$$

where μ is the shear modulus, b is the Burger vector, ν is the Poissons ratio, r_1 is the radius of the elastic strain field, and r_0 is the radius of the core. Taking $\mu = 13.5 \cdot 10^{11} \text{ dynes}/\text{cm}^2$ at 800°C (ref. 22), $\nu = 0.35$ (ref. 23), $b = 2.73 \cdot 10^{-8} \text{ cm}$ for tungsten, $r_1 = 1/\rho$, where ρ is the dislocation density $= 1 \cdot 10^8/\text{cm}^2$, and $r_0 = 10^{-7} \text{ cm}$ ²¹, the strain energy of an edge dislocation in tungsten is about $9 \cdot 10^{-4} \text{ erg}/\text{cm}$. Estimates for the energy of a single dislocation in copper²¹ and nickel²⁴ are $5 \cdot 10^{-4} \text{ erg}/\text{cm}$ and $7 \cdot 10^{-4} \text{ erg}/\text{cm}$, respectively. The value estimated for tungsten, when combined with the difference in dislocation density of $4 \cdot 10^8 \text{ cm}/\text{cm}^3$, yields $360 \cdot 10^3 \text{ ergs}/\text{cm}^3$ for the difference in strain-energy density. The only similar quantitative value available in the literature which can be compared with the present estimate comes from the work of DUNN AND AUST¹⁸, who studied quantitatively the various energies involved in stain-induced grain boundary migration in a bicrystal sheet of silicon ferrite. The value for the difference in strain-energy density deduced by them when the net driving force was zero is $42 \cdot 10^3 \text{ ergs}/\text{cm}^3$, which is almost one order of magnitude smaller than the present estimate of $360 \cdot 10^3 \text{ ergs}/\text{cm}^3$ in tungsten. Therefore, the relatively large value deduced in the present experiment is sufficient to account for the extensive strain-induced grain boundary migration observed.

Mechanical properties

It can be shown readily that the recovery of yield stress was not affected by the decrease in dislocation density with increase in annealing temperature. Increasing

the annealing temperature from 800°C to 1300°C decreased the dislocation density from $\sim 2 \cdot 10^8/\text{cm}^2$ to $\sim 1 \cdot 10^8/\text{cm}^2$. The contribution to shear stress σ from a dislocation density ρ can be calculated from the equation $\sigma = 0.1 Gb/\rho^{21}$. Inserting appropriate values into the equation, one finds that the difference in yield stress in tension for a difference in dislocation density of $1 \cdot 10^8/\text{cm}^2$ is only about 350 p.s.i. This is well within the experimental accuracy and hence provides further confidence on the observed dependence of yield stress on subgrain size.

The value for k_Y found in the present experiment can be compared with similar values determined for grain size in other b.c.c. metals. In general, k_Y , or k_Y/μ , is greater for metals having high ductile-brittle transition temperatures than for metals having low transition temperatures¹². At room temperature, for example, k_Y is $3.8 \cdot 10^6$ dynes/cm^{3/2} for columbium²⁵ and is $1.7 \cdot 10^8$ dynes/cm^{3/2} for molybdenum²⁶. (The value of k_Y for columbium determined by ADAMS *et al.*²⁵ is multiplied here by $\sqrt{2}$ since in their experiment $2d$ was taken as the grain diameter.) Since the transition temperature of tungsten is about 300°C higher than that for molybdenum, the present value of $3.3 \cdot 10^7$ dynes/cm^{3/2} appears to be very low. It is not reasonable to attribute this to the relatively high test temperature used in the present experiment (600°C) because k_Y for grain size has been found to be relatively insensitive to test temperature (k_Y increases by a factor of only 2-2½ from 25°C to -196°C)^{25,27}. The present value of k_Y for subgrain size, however, is in agreement with the recent determination of k_Y for subgrain size in iron by BALL²⁸. He found that k_Y for subgrain size is lower than k_Y for grain size in iron and attributed this difference to the relative strength of grain boundaries and subgrain boundaries. These results suggest that the low values of k_Y for subgrain size may be a general behavior of the b.c.c. metals.

Since the Petch equation was derived on the basis that the grain boundaries act as barriers for dislocation pile-ups¹⁰, the existence of the same type of relationship between the lower yield stress and subgrain size found in the present experiment suggests that the subgrain boundaries behave in much the same way as grain boundaries in acting as barriers for dislocation pile-ups. It has been shown experimentally in zinc single crystals by GILMAN²⁹ and by WEISSMANN *et al.*³⁰ that asymmetrical low-angle boundaries are effective barriers for pile-up dislocations. Such boundaries are expected in a heavily deformed material as shown by WEISSMANN in nickel and nickel alloys³¹. On the basis of the current theories of brittle fracture^{12,32} the embrittlement in tungsten which accompanies primary recrystallization can be explained without invoking the classical idea of a grain boundary film of impurities. In a sample annealed at a relatively low temperature, *i.e.*, 800°C, the fine subgrains only permit dislocation pile-ups of small size and give rise to a high effective surface energy for crack propagation (owing to the irreversible work done at "river markings")^{12,32,33}. As the annealing temperature increases the coarser subgrains allow dislocation pile-ups of larger sizes and the effective surface energy decreases, thus promoting brittleness. Upon primary recrystallization, the recrystallized grains become more than one order of magnitude larger in size than the subgrains prior to recrystallization, so that the transition temperature increases abruptly. Therefore, the increase in the transition temperature which accompanies recrystallization in tungsten can be regarded simply as a grain-size effect. A recent experiment by HARMON AND FORGENG³⁴ supports this view. For recrystallized tungsten having the same grain size, they found that specimens having very fine subgrains with diffuse subboundaries had a lower ductile-

brittle transition temperature than those having coarse subgrains with sharply defined subboundaries.

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APPENDIX

Observations were made on tungsten single crystals to secure evidence that the etch-pits developed by the KOH electrolytic etch locate the sites of emergence of dislocations. Some of the results are described briefly in the following:

(a) When the etch-pits were removed by electropolishing and the specimen re-etched, etch-pits reappeared at the same locations. Furthermore, upon successive etchings for various periods of time, the etch-pits were enlarged in size but no additional etch-pits were developed.

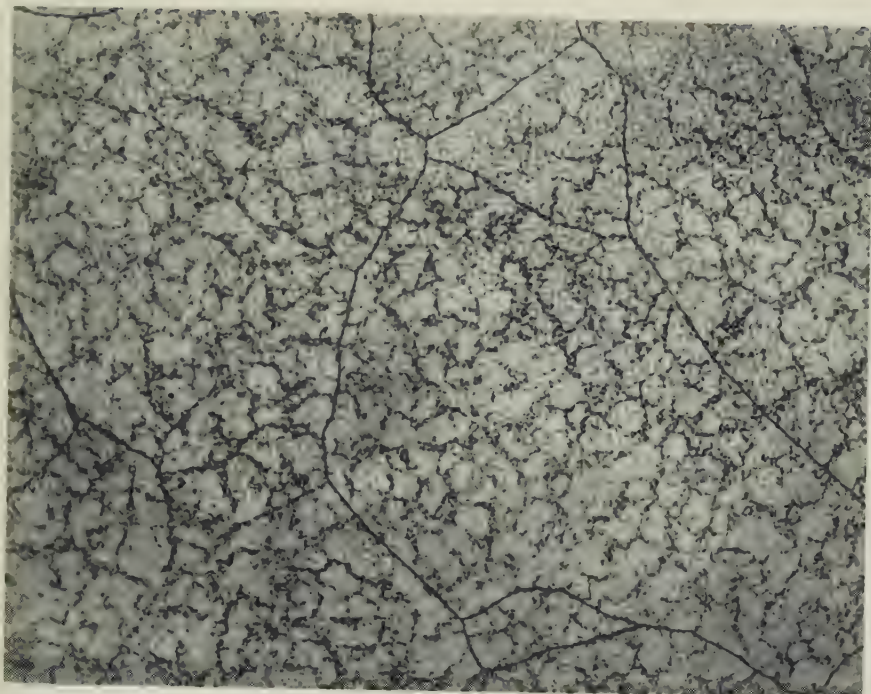


Fig. 9(a). A (100) single crystal etched electrolytically with 5% KOH solution. ($\times 150$).

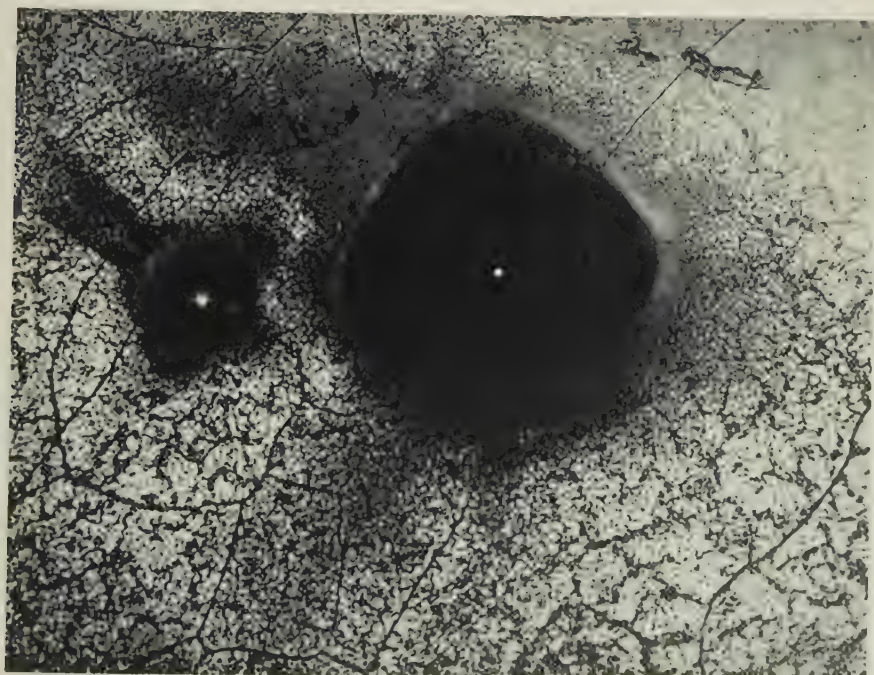


Fig. 9(b). Same as Fig. 9(a) but re-etched after indentations were made. ($\times 150$)

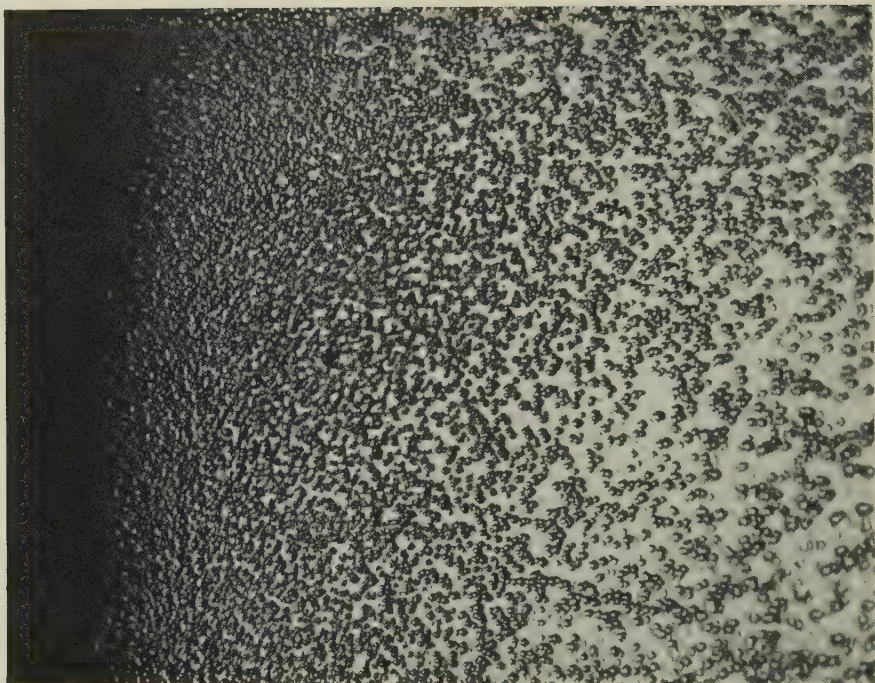


Fig. 9(c). Same as Fig. 9(b). ($\times 1000$)

(b) A single crystal having a (100) surface, (determined by Laué X-ray back reflection) was etched to develop etch-pits, as shown in Fig. 9a. All the boundaries in this sample could be resolved into rows of closely spaced etch-pits at a magnification of $3,000\times$. Diamond pyramid indentations were made on the surface and the specimen was re-etched. Fig. 9b shows the high density of new etch-pits developed by the second etch surrounding two indentations, corresponding to dislocations generated by the indentations. That the density of etch-pits decreases gradually away from an indentation is shown in Fig. 9c, the dark area on one side of this photomicrograph being a part of an indentation.

(c) In single crystals grown by electron beam melting, striation boundaries consisting of closely spaced etch-pits were developed by the etch. When Laué X-ray back reflection photographs were taken with the X-ray beam focusing on areas free of striation boundaries the Laué spots were sharp; when the X-ray beam was focused on areas containing striation boundaries the Laué spots become "split", indicating the presence of low-angle boundaries.

(d) When single crystals were deformed in tension at subzero temperatures, slip traces were formed on the surface. Upon light polishing and etching, rows of etch-pits were developed along the original slip traces. That etch-pits were developed on planes both parallel and normal to the slip direction suggests that both edge and screw dislocations are being etched.

The observations discussed above are considered as sufficient evidence that the observed etch-pits in the present experiments are indeed dislocation etch-pits.

LIQUID OXIDE PHASE SINTERING OF MOLYBDENUM AND TUNGSTEN

W. H. LENZ AND J. M. TAUB

Los Alamos Scientific Laboratory, University of California, Los Alamos, N.M. (U.S.A.)

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SUMMARY

In the hydrogen sintering of Mo and W at about 1700°C, compacts containing minor amounts of TiO_2 combined with UO_2 or ThO_2 will permit the sintered density to approach theoretical. The combination of these oxides appears to result in a phase which is liquid at the sintering temperature, and wets Mo and W.

INTRODUCTION

During an investigation on the powder rolling of Mo, the effect of additives such as SiO_2 , TiO_2 , ThO_2 and UO_2 was noted with respect to the high temperature recrystallized grain structure of the hot rolled sheet. At a later date some of these "doped" Mo

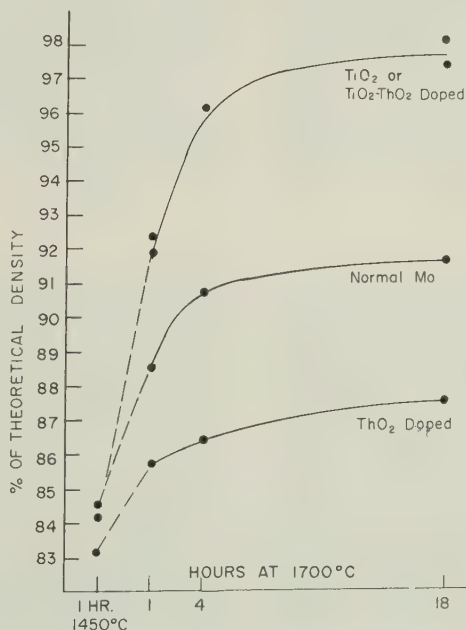


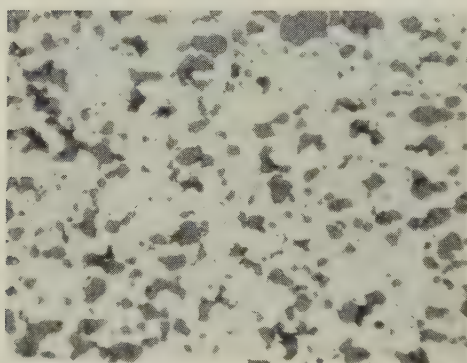
Fig. 1. Sintered density of normal Mo-20 vol.% UO_2 mixture compared with similar "doped" powders. All compositions placed in the same boat on each sintering run.

powders were also used in experimental work involving static pressing and sintering at 1700°C . The significant discovery here reported was first observed when a Mo powder doped with TiO_2 was mixed with a Mo- UO_2 powder, pressed at 60 t.s.i. and sintered at 1700°C : the resulting sintered density was much higher than when the separate powders were sintered. It appeared logical to also try such "binders" in compositions based on Mo, W, and W- UO_2 .

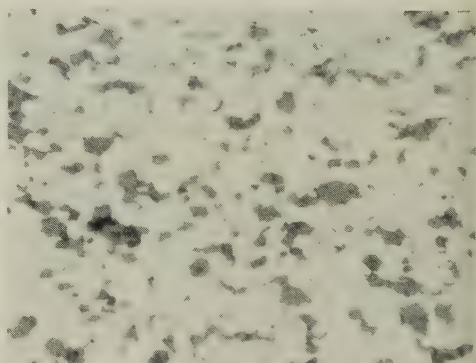
SINTERING Mo WITH OXIDE ADDITIVES

A small amount of an oxide phase which had evidently been liquid at the sintering temperature, and which apparently wetted the Mo, was found through metallographic examination in the composition containing TiO_2 - UO_2 . An example of the effect of this liquid phase on Mo- UO_2 base compositions is shown in Fig. 1, where the sintered density of a normal Mo- UO_2 base is compared with the density of similar materials containing additives. The difference in microstructure caused by the stimulative additive is shown in Fig. 2. The structures with the more rounded UO_2 particles (formed during sintering) are the ones which were higher in density and which contain the TiO_2 .

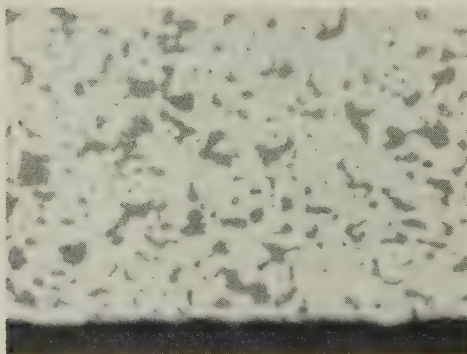
Since it is known that TiO_2 will aid the sintering of UO_2 , it might be thought that



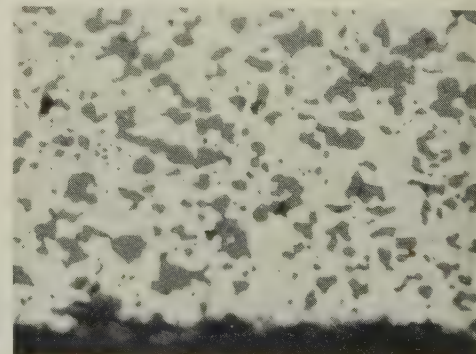
(a) Normal Mo



(b) 1% ThO_2 -doped Mo



(c) 0.87% TiO_2 -doped Mo



(d) 0.5% ThO_2 -0.44% TiO_2 -doped Mo

Fig. 2. Microstructures of Mo-20 vol. % UO_2 mixtures after 1700°C sinter, as influenced by type of additive. (500 $\times$)

this same mechanism would extend even to such mixtures diluted with 80 vol. % or more Mo. It seems somewhat absurd, however, to believe that isolated particles of UO_2 could attract each other in the presence of TiO_2 , and thus cause the Mo matrix to shrink. Furthermore, additional experiments have shown that UO_2 is not needed to cause such action.

SINTERING W WITH OXIDE ADDITIVES

In work with W, bodies of W- UO_2 powder with a TiO_2 additive were cold pressed in contact with pure W powder. During sintering, both layers achieved a high density, and metallographic examination showed that a liquid oxide phase had migrated into the pure W layer, thus proving that this UO_2 - TiO_2 liquid wets W.

TABLE I
EFFECT OF TiO_2 - UO_2 ADDITIVE ON DENSITY OF W SINTERED AT 1700°C

TiO_2 (wt. %)	UO_2 (wt. %)	W (wt. %)	% of theor. density	Remarks
0	0	100	90.9	(W powder as rec'd)
1	0	bal.	95.7*	(TiO_2 ball-milled into W powder)
1	10	bal.	100	(UO_2 added by blending)**
1	5	bal.	99.1	(UO_2 added by blending)**
1	1	bal.	97.3	(UO_2 added by blending)**
0.5	0.5	bal.	97.4	(UO_2 added by blending)**

* This increase is believed to be due to the ball-milling rather than the TiO_2 , in view of other similar tests. The W powder consisted of a 1:1 blend of powders which averaged 2.5 and 3.6 μ on the Fisher test, and contained 0.05% Ni (as a residual impurity) which apparently aided sintering. The TiO_2 was a sub-micron powder.

** The UO_2 averaged 1.2 μ on the Fisher test.

TABLE II
EFFECT OF ADDITIVE COMBINATIONS ON DENSITY OF W COMPACTS SINTERED AT 1700°C

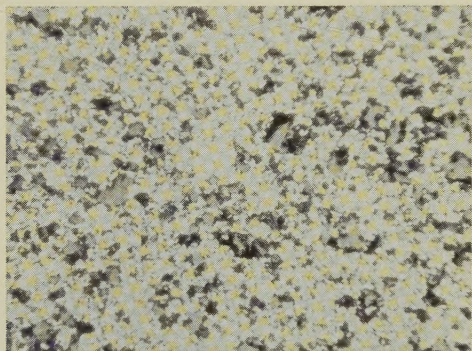
Powder composition	% of theor. density
(1) Tungsten, 2.5 μ avg., ball milled $\frac{1}{2}$ h	87.1
(2) Same as (1) plus 2 wt. % ThO_2	88.4
(3) Same as (2) plus 1 wt. % TiO_2	95.6
(4) Same as (3) plus 20 vol. % UO_2	98.5
(5) Tungsten, 2 μ , ball milled $\frac{1}{2}$ h	90.8
(6) Same as (5) with 50 vol. % UO_2 (4.5 μ)	80.0
(7) Same as (6) with 0.33% TiO_2	99.2

Table I shows the densities obtained when W powder was mixed with decreasing amounts of TiO_2 - UO_2 and sintered at 1700°C . Table II shows that ThO_2 is inert in the W- ThO_2 mixture, but stimulates sintering when TiO_2 is also present. A liquid phase also appears to form in the latter case analogous to TiO_2 - UO_2 . Figure 3 shows the change in porosity and microstructure when TiO_2 is added to a mixture of W- UO_2 - ThO_2 .

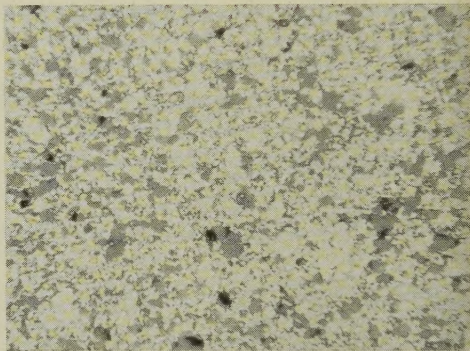
More recent work is referred to in lines 5, 6 and 7 of Table II involving W-50 vol. %

UO₂. There is a great difference in sintered density due to the TiO₂ addition. Without it the sintered density of the W-UO₂ is little better than the green density; but with 0.33% TiO₂ the final density is very near theoretical.

It must be conceded that the TiO₂ is more effective with increasing amounts of UO₂, but the particle size and degree of dispersion of the UO₂ is a factor perhaps more important than the per cent by volume. It will be seen in Table I that very high densities were achieved with 5 and 10% UO₂.



(a) Tungsten-20 vol.% UO₂ plus 2 wt.% ThO₂.
86.9% of theor. density.



(b) Same as (a) plus 1 wt.% TiO₂. 98.5% of theor. density.

Fig. 3. Microstructures of W-20 vol.% UO₂ mixtures, sintered 3 h at 1700°C, as influenced by type of additive. (500×)

DISCUSSION OF RESULTS

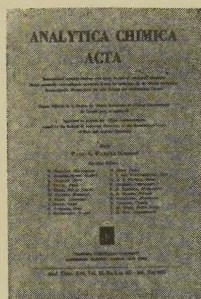
No extended exploration of the various metal-oxide systems which might show this type of reaction has been made. The reactions between Mo and W as metals and TiO₂-UO₂ or TiO₂-ThO₂ as oxides have been confirmed, however, by repeating these runs with a range of different particle-sized powders. (Alternate methods of adding the TiO₂ were also tried.) To the authors' knowledge this strong sintering action of a molten oxide on a metal-rich system has not previously been reported.

The phenomenon is not one of a liquid phase merely filling existing pores, such as might be obtained by infiltration. Rather, the additives are originally present as solids, and form a liquid eutectic at about 1550°C. This liquid has the power actually to eliminate voids to a much greater extent than would be the case if the liquid were not present. No explanation is being advanced to account for the observed effect. Solubilities of the various components, however, would probably be of a very low order. Since a strong wetting action has been demonstrated by the liquid oxide (at least in the presence of hydrogen) there may be some way in which this can influence the modification and rearrangement of the constituent grains.

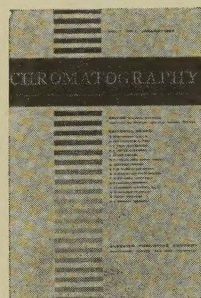
From an academic viewpoint, at least, these observations may stimulate further experiments in this field which borders on both metallurgy and ceramics.

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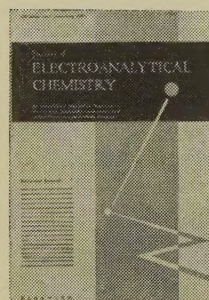
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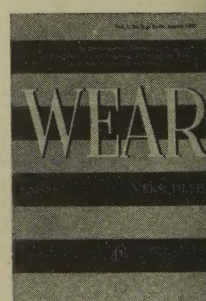


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